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Single and mixed dithiocarbamato metal(III) complexes (Co, Rh, and Ir): Crystal and molecular structure description and interplay

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REVIEW ARTICLE

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ABSTRACT

This review focuses on the crystal and molecular structures of single and mixed dithiocarbamate ligands of cobalt, rhodium, and iridium in the +3 oxidation state. The complexities of their chelating and bridging modes come into play through modification of the substituents on the carbamate nitrogen atoms of the ligands and additional coordination of secondary phosphino-containing ligands, culminating in various applications such as biological, analytical, medicine, and catalysis. Other considerations include the geometrical coordination environments around the metal centres and their comparison with isostructural congeners. The distortions around the metal centres and their subsequent effects on the symmetries of bonds in the primary and secondary coordination spheres are discussed. The trans-effects of secondary P-ligands and their effects on geometrical alignment and structural stability have become valuable yardsticks in analyzing structural modifications and stabilities.

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1. Introduction

The M-S_2CNR_2 core in dithiocarbamate chemistry has proved to be of great use to synthetic and structural scientists because of the possibility of modifying the R and R' substituents in the backbone of the stable ligand framework (Scheme 1). Modification of organic substituents allows fine-tuning of the chemical properties of complexes that are fast becoming commonplace [1]. Dithiocarbamates and their derivatives are versatile chelating compounds through their sulfur atoms, resulting in central metal ions that are tetracoordinated (square planar or tetrahedral), penta-coordinated, sometimes due to dimerization, or hexa-coordinated in a regular or distorted fashion [2,8]. Interestingly, the introduction of secondary ligands along with auxiliary dithiocarbamate anions results in bridges that invariably modify the entire coordination sphere through substantial labilization to form novel products [3-5].

For example, mixed dithiocarbamate ligands and other notable P ligands, such as phosphines, phosphinites, phosphornites, and phosphites [6] have been reported to be modifiers of the underlying properties of dithiocarbamate complexes as revealed by characterization through X-ray diffraction studies [5]. Dithiocarbamates have been reported to be reliable auxiliary ligands with a very strong tendency to stabilize Co(III)-P bonds [4]. Moreover, the supramolecular chemistry of hydrogen bonding O⋯H-P and agnostic M⋯H-P interactions are borne out of the stable mononuclear secondary phosphine complexes. These complexes also provide rational synthetic pathways for heterometallic and homometallic phosphide-bridged di- or polynuclear complexes; a feat attained by the deprotonation of the phosphor ligands by coordination [7].

Dithiocarbamates in their single and mixed forms are quite versatile. They have been used in the treatment of sarcoma cells and alcoholism [8]; a feat that has brought diethyldithiocarbamate to the scientific limelight as the active metabolite of disulfiram, an anti-alcoholic drug [9]. The drug therapy potentials of dithiocarbamates were identified by their ability to form chelates with virtually all metals and their strong affinity for human and enzyme-based thiol groups [9].

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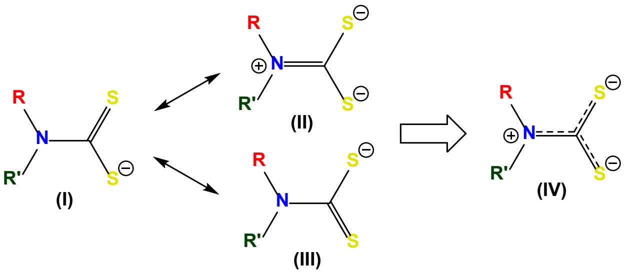
Table 1. Applications of dithiocarbamates.

Applications	**References**
Thermodynamics and kinetic studies	[7]
Treatment of Sacoma cells	[8]
Protective agent against dangerous X-rays	[8]
Treatment of alcoholism	[9]
Medicine	[10]
Metal separation via gas chromatography	[12]
Liquid-liquid extraction in analytical chemistry	[12]
Biological studies, *e.g.* anti-alkylation	[13]
Anti-HIV	[14]
Antidotes for cadmium intoxication	[15]
Catalysis	[16]
Anticancer agents	[9,17]
Internal standards determination of metals via gas chromatography	[18,19]
Photoluminescent studies	[20]



Scheme 1. Resonance structure of the typical dithiocarbamate ligand.

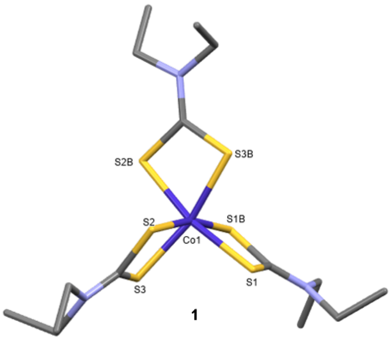


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Figure 1. The molecular structure of complex **1**.

In the last 20-25 years, dithiocarbamates have been extensively studied as anticancer, antiviral, antibacterial, and antifungal agents and have been used repeatedly in neurological applications with emphasis on the treatment of Alzheimer's disease. Not left out of these is the attempted use of disulfiram and diethyldithiocarbamate in clinical trials as antiviral agents against the human immunodeficiency virus HIV-1 and variable HIV-RNA (ribonucleic acid) [9].

Dithiocarbamates play specific catalytic roles in the vulcanization of rubber and in the radical chain transfer of polymerization reactions [10]. They have also shown extensive use as electrochemical sensors; a technique that is simpler and cheaper compared to spectroscopy and chromatography. Their extensive use has led to the development of analytical quantification of the main metabolites; ethylene thiourea and propylene thiourea, which are the main sources of the toxic nature of dithiocarbamates [11].

The coordination chemistry of cobalt, rhodium and iridium is favored because of (i) the stability of their +3 oxidation states, (ii) the formation of varying coordination geometries by coordinating with dithiocarbamate ligands, (iii) the formation of various coordination geometries from the mixed ligand complexes of dithiocarbamates and phosphorus binding ligands, and (iv) the utilization of these geometrically aligned complexes to develop novel complexes with enormous scientific applications (Table 1 [7-10,12-20]).

The last 5-6 decades have witnessed rigorous research that highlights the significance of dithiocarbamate chemistry at the crystal and molecular levels [21-23]. Previous publications on dithiocarbamate complexes have guided us in this review, wherein we present single and mixed dithiocarbamate ligands of Co(III), Rh(III), and Ir(III) in light of their chelating and bridging coordination modes, the effects of substituent change on the carbamate N on the overall structural patterns, the geometric alignment around the metal of focus and how symmetric and asymmetric bonds affect geometry and association in the primary and secondary coordination spheres. The modification of bonds (lengthening or shortening) via trans effects of specific functional groups, especially the P-ligands, will be discussed extensively.

This review presents the varying structures of the triad of dithiocarbamates and their mixed ligand derivatives, which is valuable in analyzing their structural stability. Based on the foregoing, this review will focus on the crystal and molecular structures of single and mixed ligand (P-ligand) complexes of Co, Rh, and Ir in the +3 oxidation states which were obtained via search of the Cambridge Structural Database (CSD) [24]. These structures are subsequently extracted with Mercury [25], a conventional crystallographic visualization tool (Table 2) [4,5,8-20,26-52].

Table 2. Refcodes, IUPAC names and unit cell parameters of complexes **1-18**.

Complexes	Refcodes	IUPAC names	Unit cell parameters	Ref.
1	ETDCCO	Tris(diethyldithiocarbamato)cobalt(III)	a = 14.087(8) Å, b = 10.308(4) Å, c = 17.049(11) Å, β = 111.0(8)°	[8]
2	LOYFEK	Tris(dipropyldithiocarbamato)cobalt(III)	a = 10.185(1) Å, b = 10.185(1) Å, c = 51.807(4) Å, α = 90°, β = 90°, γ = 120°	[12]
3	MIJPEA	Cis-bis(diphenylphosphine)-bis(*N,N*-dimethyldithio carbamato-S,S')-cobalt(III) tetrafluoroborate acetonitrile diethyl ether solvate	a = 19.359(1) Å, b = 11.110(<1) Å, c = 20.642(1) Å, α = 90°, β = 115.83(< 1)°, γ = 90°	[5]
4	MIJPIE	Trans-bis(diphenylphosphine)-bis(*N,N*-dimethyldithio carbamato-S,S')-cobalt(III) tetrafluoroborate	a = 19.507(4) Å, b = 14.529(5) Å, c = 14.445(3) Å, α = 90°, β = 122.20(1)°, γ = 90°	[5]
5	MTHCCO	Tris(*N,N*-dimethyldithiocarbamato)cobalt(lll)	a = 13.992(7) Å, b = 9.770(3) Å, c = 13.555(6) Å, β = 101.50(4)°	[31]
6	MTHCCO01	Tris(*N,N*-dimethyldithiocarbamato)cobalt(III)	a = 13.5553(7) Å, b = 9.7636(5) Å, c = 17.4440(11) Å, α = 90°, β = 128.180(4)°, γ = 90°	[20]
7	TDTCCO	Tris(dithiocarbamato)cobalt(III)	a = 16.300(2) Å, b = 10.056(2) Å, c = 7.095(1) Å, α = 90°, β = 101.00(20)°, γ = 90°	[32]
8	YOFBUQ	Bis((1,2-bis(diphenylphosphino)ethane)-bis(*N,N*-diethyldithiocarbamato)-cobalt(II)) (μ_2-1,2-bis(diphenyl phosphinoyl)ethane-O,O')-hexachloro-di-zinc chloroform solvate	a = 11.732(1) Å, b = 16.526(1) Å, c = 18.852(1) Å, α = 64.97(< 1)°, β = 80.62(< 1)°, γ = 86.46(< 1°)	[39]
9	PIDKIW	Cis-bis((dimethyldithiocarbamato-S,S')-(4-ethyl-2,6,7-trioxa-1-phosphabicyclo(2.2.2)octane-P))-cobalt(III) tetrafluoroborate	a = 23.867(3) Å, b = 17.583(2) Å, c = 15.243(2) Å, α = 90°, β = 103.97(2)°, γ = 90°	[4]
10	PIDKOC	Tetrakis(trimethylphosphite)-(piperidyldithiocarbamate-S,S')-cobalt(III) bis(tetrafluoroborate)	a = 11.259(2) Å, b = 23.865(4) Å, c = 14.293(2) Å, α = 90°, β = 83.69(1)°, γ = 90°	[4]
11	GIJDEI	Catena-(bis(μ_2-Bromo)-(μ_3-(N,N-diethyldithiocarbamato-S,S,S',S'))-bis(μ_2-(N,N-diethyldithiocarbamato-S,S,S'))-cobalt(III)-di-copper(I) acetonitrile solvate)	a = 18.910(20) Å, b = 14.583(4) Å, c = 13.705(8) Å, α = 90°, β = 118.82(6)°, γ = 90°	[45]
12	GIJDIM	catena-(tris(μ_3-N,N-Tetramethyleneldithiocarbamato-S,S,S',S')-tris(μ_2-iodo)-cobalt(III)-tri-copper(I))	a = 23.637(10) Å, b = 23.637(10), c = 23.637(10) Å, α = 90°, β = 90°, γ = 90°	[45]
13	PYTCCO01	Tris(pyrrolidine-1-carbodithioato)cobalt(III)	a = 28.984(15) Å, b = 14.416(2) Å, c = 16.206(15) Å, α = 90°, β = 104.20(5)°, γ = 90°	[26]
14	JERFER	Tris(*N,N*-dibenzyldithiocarbamato)cobalt(III)	a = 11.851(6) Å, b = 29.920(8) Å, c = 12.395(3) Å, α = 90°, β = 97.74(4)°, γ = 90°	[26]
15	JERDUF	Tris(*N,N*-diisopropyldithiocarbamato)cobalt(III)	a = 13.155(6) Å, b = 13.155(6) Å, c = 13.155(6) Å, α = 58.59(3)°, β = 58.59(3)°, γ = 58.59(3)°	[26]
16	MOTCRH	Tris(morpholinodithiocarbamato)rhodium(III)	a = 13.343(4) Å, b = 10.596(1) Å, c = 11.191(1) Å, α = 114.20(1)°, β = 103.18(2)°, γ = 101.29(2)°	[48]
17	TEDCRH	Tris(diethyldithiocarbamato)rhodium(III)	a = 18.07(3) Å, b = 8.276(3) Å, c = 15.80(1) Å, β = 96.35(4)°	[50]
18	EDTCIR	Tris(diethyldithiocarbamato)iridium(III)	a = 14.071(5) Å. b = 10.477(3) Å, c = 16.980(5) Å, β = 108.61(2)°	[52]

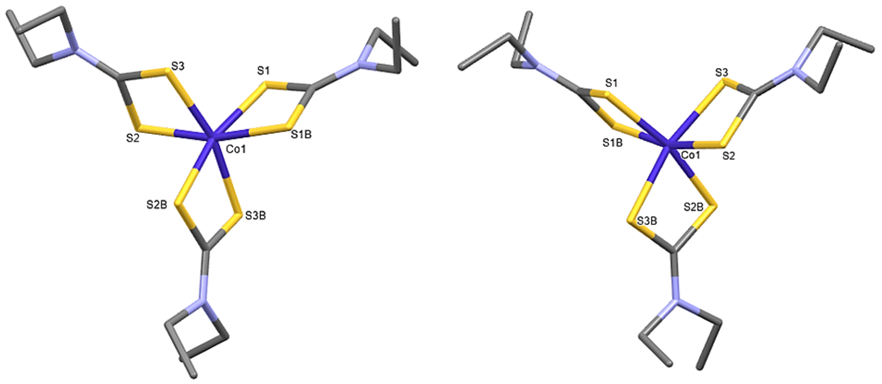

Figure 2. The stereo pair of complex **1** with its 2-fold axis stretching through Co, C, and carbamate N [8].

2. Single dithiocarbamato and mixed ligand M(III) complexes

2.1. Co(III) complexes

Tris(diethyl(dithiocarbamato)-cobalt (III) (**1**, Figure 1) belongs to the monoclinic crystal system with four molecules in the unit cell. The observed extinctions, hkl (h+k≠2n) and hol (l≠2n) are in agreement with the space groups *C*2/*c* and *Cc*, respectively [8]. With a space group of *C*2/*c*, the entire molecule is expected to possess a two-fold symmetry axis such that the central Co occupies a special position (4e) of the space group. The Co atom bisects one dithiocarbamate ligand, while all atoms in the second dithiocarbamate ligand lie in general positions and subsequently take turns to generate the third dithiocarbamate ligand via rotation about the 2-fold axis (Figure 2).

It is obvious that the six sulfur atoms around the cobalt center form a geometry that is quite distorted from the regular octahedron [as seen in the S-Co-S bond angles of 166.21(12)° and 166.51(9)°. These distortions are attributed to the imposition of constraints on the entire geometry of the molecule by the rigidity of the dithiocarbamate ligands and the small bites of the metal centers, which are S-Co-S = 76.50(14)° and 76.05(10)°. In comparison with other similar complexes such as $Fe(CO)_2[S_2CN(CH_2)_5]_2$ [8], $Ni[S_2CN(C_2H_5)_2]_2$ [27], $Cu^{II}[S_2CN(C_2H_5)_2]_2$ [28] and $Zn^{II}[S_2CN(CH_3)_2]_2$ [8], the S-C, C-N and N-C_{alkyl} bond distances are in close alignment except for the M-S bonds whose variations were expected to align with the ionic radii of the central metal ions, but this was never the case. For instance, the longer Fe-S bond compared to Co-S bond does not align with the difference in their ionic radii but reflects the differences in their individual charges. Ni(II), Cu(II), and Zn(II) on the other hand, possess smaller M-S bonds compared to

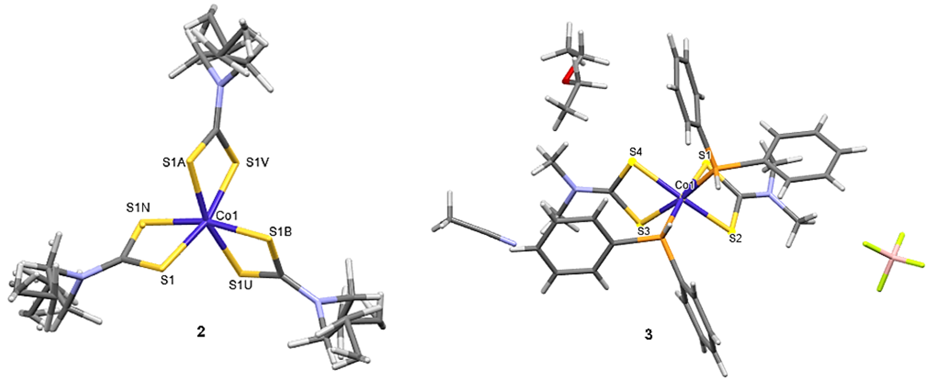

Figure 3. Molecular structure of complexes **2** and **3**.

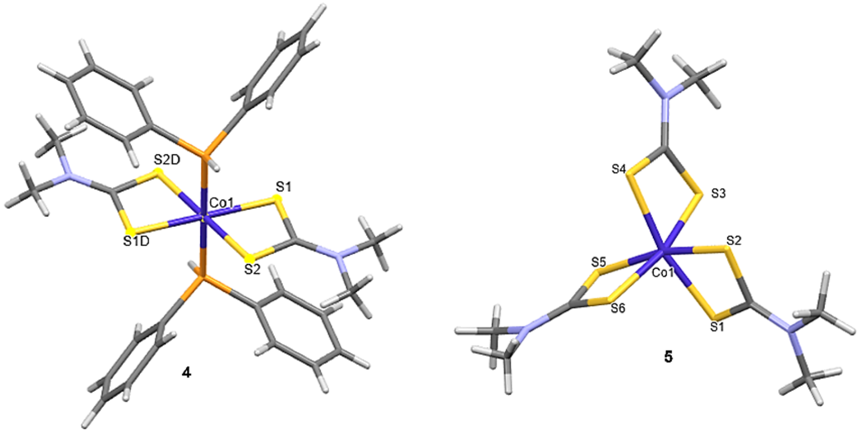

Figure 4. Molecular structure of complexes **4** and **5**.

those of Co and Fe despite possessing higher ionic radii of 0.69, 0.72 and 0.74 Å (compared to 0.64 Å for Fe(II) and 0.63 Å for Co(II)). One important factor that accounted for the variation in M-S bonds is the coordination about the metal centre. Fe(III) and Co(III)^{I} in complex **1** (Figure 1) are hexacoordinated, while the Ni, Cu, and Zn complex are tetracoordinated with Ni-S bond distances in the range of 2.1-2.3 Å compared to 2.4-2.6 Å reported for hexacoordinated Ni-S [8]. Similarly, the M-S bond distances in the hexacoordinated Cu(II) and Zn(II) are 0.2-0.3 Å longer than those found in their tetracoordinated congeners. The 1.303 and 1.315 Å reported for the C-N bonds are strong indications of a high degree of double bond character initiated by the canonical form (II in Scheme 1). The canonical structure also supports identical C-S bond lengths through the trigonal *sp*^{2} angles of 117.78-121.11° around carbamate N atoms and the planarity of CoS_2CN fragments [29]. Complex **1** has six similar complexes which also crystallized in the *C*2/*c* space group [24]. With emphasis on one of the variants of complex **1** (ETDCCO06) [30], H⋯S contacts in the range 2.979-2.998 Å with methyl- and methylene C-H donors.

Co^{III} tris(dipropyldithiocarbamate) (**2**, Figure 3) crystallizes in the *R*-3*c* space group of the rhombohedral crystal system. Its unit cell is made up of six discrete monomeric molecules such that the Co ion is the intersection of the mutually perpendicular 3-fold and 2-fold axes [12]. The central Co is coordinated bidentately to three [S_2CNPr_2] ligands that are related by the 3-fold axis. The distorted hexacoordinated geometry around the central Co is formed by the meridional arrangement of the six S atoms around it. Its distortion is attached to the enforced configuration of the 4-membered chelating ring system resulting in average Co(III)-S distance of 2.262(3) Å, S-Co-S angles of 165.74(11) and 166.5(2)° and the imposition of constraints on the entire molecule by the rigidity of the ligands and the small S-Co-S "bites" of 76.34(11) and 76.2(2)° [12]. The distortions in complex **2** are not far-fetched and have been observed in other derivatives of the form [$Co(S_2CNR_2)_3$], where R = Et, ^{i}Pr and CH_2Ph [8,26]. The high degree of double bond character in complex **2** is responsible for the short N-C bond distance of 1.340(9) Å. The crystal lattice of complex **2** is dominated by H⋯H interactions of distance 2.199 Å with the methylene donor.

The cis-[$Co(DTC)_2(PHPh_2)_2$]$BF_4 \cdot CH_3CN \cdot 0.5Et_2O$ (where DTC = *N,N*-dimethyl dithiocarbamate , $PHPh_2$ = diphenylphospine) (**3**, Figure 3) crystallizes in the *P*2/*n* space group of the monoclinic crystal system [5]. Its P-H bond distances of 1.37(3) Å and 1.36(2) Å are consistent with ^{1}H NMR measurements. The two phenyl rings are oriented in such a way that the intramolecular interaction between the two steric $PHPh_2$ ligands is reduced while the DTC plane and one of $PHPh_2$'s phenyl interact through stacking. The Co-P bond distances of 2.2340(6) and 2.2258(7) Å are shorter than those observed in cis-[$Co(DTC)_2(PMe_2Ph)_2$]PF_6 (where $PMePh_2$ is sterically less bulky but more basic than $PHPh_2$) with Co-P bond distances of 2.2795(6) and 2.2637(7) Å [6]. The P-Co-P angle of 90.51(2)° is clearly smaller than what is obtainable in cis-[$Co(DTC)_2$(P-ligand)$_2$]$^+$ variant of complexes [4,6]. The crystal lattice of complex **3** is dominated by H⋯F, H⋯B, H⋯O, and H⋯N interactions with methyl-C-H. aromatic-C-H and P-H donors, while the O, F, and N acceptors are from diethyl ether, tetrafluoroborate anion, and acetonitrile, respectively.

Trans-[$Co(DTC)_2(PHPh_2)_2BF_4$] (**4**, Figure 4) (isomer of complex **3**) crystallizes in the *C*2/*c* space group of the monoclinic crystal system [5]. Its equal P-H bond distances of 1.21(3) Å are remarkably shorter than P-H bond distances of 1.37(3) and 1.36(2) Å in the cis-isomer. Its Co-S bond distance and bite angles in the DTC ligand align well with those of trans-[$Co(DTC)_2PMe_{3-n}Ph_n$]BF_4 (n = 1, 2, and 3) [4,6]. Its Co-P distances of 2.276(1) Å are much shorter than those available

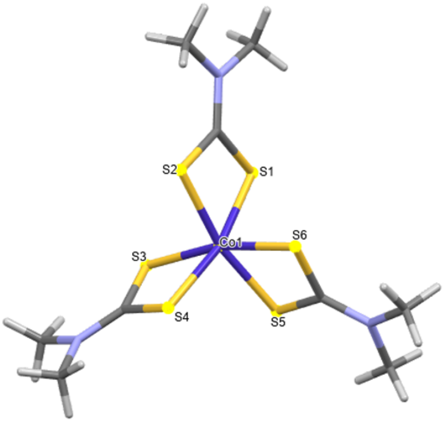

Figure 5. Molecular structure of complex **6**.

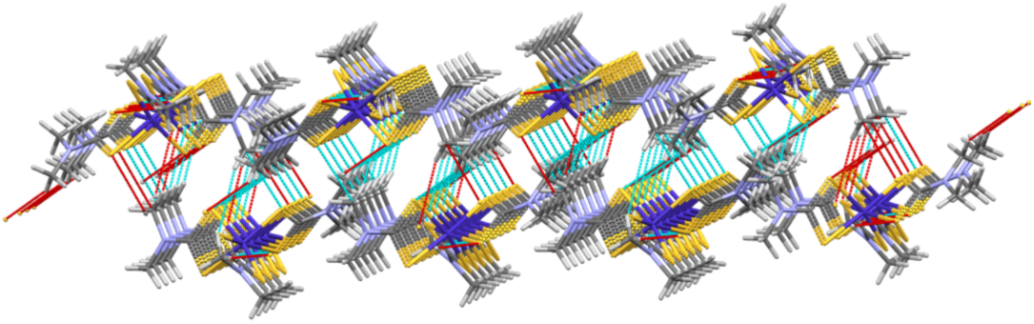

Figure 6. Crystalline 3D aggregate generated from complex **6** [20].

in trans-[Co(DTC)$_2$PMe$_{3-n}$Ph$_n$]BF$_4$ despite that PMe$_2$Ph and PMe$_3$ exhibiting sterically smaller and stronger σ-donor capabilities compared to PHPh$_2$. Trans interactions or influence in phosphine complexes are indicated by the short Co-P bond distances. Several mixed ligand Co(III) dithiocarbamate complexes incorporating phosphines, phosphinites, phosphornites, and phosphites have become common coupled with the trans influence they exhibit on structural and molecular trends [3-6]. The crystal lattice of complex **4** is dominated by aromatic-C···C-aromatic methyl-C···F, aromatic-C-H···F with the acceptor F atom emanating from the tetrafluoroborate anion.

Tris(*N,N*-dimethyldithiocarbamato)cobalt(III) (**5**, Figure 4) crystallizes in the $P2_1/n$ space group of the monoclinic crystal system [31]. It has three dithiocarbamate ligands that are octahedrally coordinated to the Co center through the dithiocarbamate sulfur atoms. The ligand dimensions are in alignment with crystallographic expectations while the complex assumes a good approximation with 32 symmetry. The Co atom lies in nearly the plane of the ligand with very small deviation of 0.18(3), 0.02(1) and 0.05(1) Å from the planes of the three ligands. The CoS$_6$ coordination polyhedron has a Co-S mean bond distance of 2.264 Å that is intermediate between what was observed for [Co(S$_2$CNH$_2$)$_3$] (2.275 Å) [32] and [Co(S$_2$(NEt$_2$)$_3$] (2.258 Å) [33]. The intermediacy of the Co-S bonds is attached to the location of [Co(S$_2$CNH$_2$)$_3$] and [Co(S$_2$(NEt$_2$)$_3$] on the crystallographic 3-fold and 2-fold axes resulting in increased and decreased bond lengths, respectively. The 'bites' of the S-Co-S angles are in the range 76.25-76.46°. Its C-S bond distances in the range 1.7015-1.7085 Å, which are intermediate between single C-S and double C=S bonds, are suggestive of substantial charge delocalization over the NCS$_2$Co plane. The canonical form of complex **5** is likely to be responsible for its high degree of double bond character as revealed by C-N bond distances of 1.3147, 1.3267 and 1.3189 Å. It lacks the n-fold axis relation but is driven by the trigonal symmetry. Raston *et al.* [32] also suggested that the disparities in the Co-S distances could be as a result of the variation in the sulphur environment around the Co centre. Its crystal lattice is dominated by short intermolecular $_{\mathrm{sp3}}$C···S contacts and hydrogen bond interactions of the form $_{\mathrm{sp3}}$C-H···S contacts. The $_{\mathrm{sp3}}$C···S contacts of 3.425 Å were repeated throughout the lattice, while H···S contacts of distances 2.965, 2.944, and 2.830 Å were recorded for the hydrogen bond interactions. The short intermolecular H···S contacts were not worth reckoning with because the positions of the H atoms were not accurately determined.

[Co(ddc)$_3$] (**6**, Figure 5) is a neutral coordination complex just as complex **5**, where the ddc is obtained from *N,N*-dimethyldithiocarbamic acid Hddc [20]. It crystallizes in the $P2_1/c$ space group (compared to its complex **5** polymorph which crystallizes in the $P2_1/n$ space group) of the monoclinic crystal system. The cobalt center is distortedly hexacoordinated to six sulfur atoms of *N,N*-dimethyldithiocarbamic acid; two sulfur atoms are in the axial position and four in the equatorial plane. Its asymmetric unit contains three molecules of *N,N*-dimethyldithiocarbamic acid and one Co(III) ion. Each Hddc ligand is bidentate and chelates to the cobalt centre forming a 4-membered [CS$_2$Co] ring that is similar to that obtained in [Co{S$_2$CN(CH$_2$CH$_2$CH$_2$NMe$_2$)$_2$}$_3$ [34]. The Co-S bond distances in the CS$_2$Co ring are in the range 2.2531(12)-2.2734(13) Å and are slightly stronger than the range 2.2645(15)-2.2766(15) Å observed in [Co(ecpzdtc)$_3$ where ecpzdtc is 1-ethoxycarbonyl piperazine-4-carbodithioate [35] as well as that obtained in complex **5**. The 'bites' of the S-Co-S angles are in the range 76.24(5)-76.61(5)° and are quite similar to the range obtained for complex **5**. The C-S bond distances in the range 1.701(4)-1.712(6) Å are quite similar to those of complex **5** and are intermediate between single C-S and double C=S bonds, suggesting substantial charge delocalization in the NCS$_2$Co plane [20].

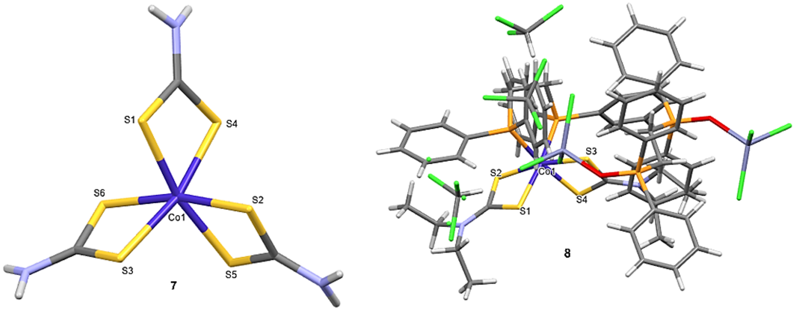

Figure 7. Molecular structures of complexes **7** and **8** with its distorted structure and chloroform solvates.

Figure 8. Molecular structure of complexes **9** and **10**.

Complexes **5** and **6** share quite similar canonical forms which are likely to be responsible for their high degree of double bond character, as revealed by complex **6**'s C-N bond distances of 1.319(5), 1.319(8) and 1.327(7) Å. As in complex **5**, the $_{sp3}$C⋯S contacts, although shorter by 0.010 Å, and the $_{sp3}$C-H⋯S interactions with H⋯S contact distances of 2.897, 2.992 and 2.856 Å were integral parts of the 3D aggregate formed from complex **6** (Figure 6). From a symmetry perspective, complexes **5** and **6** possess the 2-fold screw axis with direction [0,1,0] at ¼, y, ¼ for complex **5** and 0, y, ¼ for complex **6.** They both possess inversion centres at [0,0,0], while their glide planes are perpendicular to [0,1,0] with the glide component [½,0,½] for complex **5** and [0,0,½] for complex **6**.

Tris(dithiocarbamato)cobalt(III) (**7**, Figure 7) crystallizes in the monoclinic $P2_1/a$ space group [32]. Its crystal structure description was triggered by the determination of the structure of $[Ni(CS_2NH_2)_2]$ with a mean C-N bond distance of 1.37(5) Å [36]. It is a discrete molecule with three planar ligands that are coplanar with the Co center. The arrangement of the three planar ligands around the Co center results in a D_3 three-bladed propeller. The geometry of the $CoS_6C_3N_3$ fragment of the molecule is in agreement with crystallographic expectations and is similar to that extracted from $[Co(CS_2NEt_2)_2]$ [33]. In its CoS_6 coordination polyhedron, the mean Co-S bond distance of 2.275 Å is longer and weaker than 2.258 Å found in the diethyl derivative [8,33].

The reason for the disparity is attached to the diminished accuracy of the crystal data [36-38], where the M-S bond distance is a function of the crystal field components of the disubstituted ligand which tends to decrease by 0.03 Å on switching from a strong field ligand such as $[CS_2N^iPr_2]^-$ to a weak field ligand such as $[CS_2NH_2]^-$. The disparities could alternatively be connected to the varying thermal motion of the structures, with the unsubstituted compound expected to possess less thermal motion than the diethyl derivative. In Complex **7**, the systematic distortion of the CoS_6 coordination core reduces the symmetry from D_3 to C_3, resulting in asymmetric Co-S bond distances as well as S-Co-S bond angles. The asymmetry in this case culminates in an increase in the number of short S⋯H interactions. Trigonal pyramidal distortions were observed about carbamate N atoms and these may emanate from hydrogen bonding interactions, which expose the nitrogen to sp^3 orbital contribution. The difficult scattering model of the hydrogen atoms of complex **7** is responsible for the shorter mean C-S bond distance of 1.70(2) Å compared to those of the accurately solved diethyldithio- carbamate crystal, which is in the range 1.71-1.73 Å. Likewise, the mean C-N bond distance of 1.32(1) Å is even much shorter than that observed in accurately solved diethyldithio-carbamate. These data lend fact to the wrong and longer than normal estimation of 1.37(5) Å for the C-N bond in $[Ni(CS_2NH_2)_2]$. One reason for the over-estimation is the bias of the position of carbamate nitrogen around hydrogen atoms [32]. Its crystal lattice is dominated by short intermolecular N-H⋯S, S_2C⋯H-N and S⋯S, $_{sp3}$C⋯S contacts.

Complex **8**'s (Figure 7) crystal structure is part of a 2:1 salt of the cation $[Co(S_2CNEt_2)_2(dppe)]^+$ and anion $[Cl_3ZnO{:}O(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]^{2-}$ [39]. It crystallizes in the triclinic *P*-1 space group. The salt $[Co(S_2CNMe_2)_2(dmpf)][BPh_4]$ [3], where dmpf = 1,1'-bis(dimethylphosphino)ferrocene, shares close similarities with complex **8**. They both possess similar Co-S and Co-P bond distances. The trans influence of the P-donor of the ligand is reflected in the Co-S trans to P being longer than the Co-S trans to S by 0.03 Å [8]. The bite angle around the cobalt centres of the dithiocarbamate ligands for the two complexes is ~76° while dmpf's bite angle of 102.3(1)° around the Co(III) centre is greater than dppe's 87.01(2)°. The anion $[Cl_3ZnO{:}O(Ph)_2PCH_2CH_2P(Ph)_2{:}OZnCl_3]^{2-}$ is peculiar for its bridging 1,2-bis(diphenylphosphinoyl)ethane ligand. However, such bridging coordination patterns have previously been reported in Co(II) complexes $[CoCl_2\{O{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}O\}]_2$; a cyclic dimer [40], $[CoCl_2\{O{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}O\}]_n$, a linear polymeric complex [39] and $[Co(CO)(dppe)_2Cl_3CoO{:}(Ph)_2PCH_2CH_2P(Ph)_2{:}OCoCl_3]$; an ionic coordination salt [39]. Di(*N*,*N*-diethyldithiocarbamato)[1, 2-bis(diphenylphosphine)ethane] cobalt(III) tetrachlorocadimate $\{[Co(S_2CNEt_2)_2(dppe)]_2[CdCl_4]$ which shares a similar cation with complex **8** crystallizes in the triclinic *P*-1 space group. Its crystal lattice is dominated by a considerably distorted structure coupled with a substantial amount of chloroform solvates. Therefore, only its unit cell parameters *a* = 23.6388 10) Å, *b* = 11.4468(4) Å, *c* = 47.2679(2) Å, and β = 104.0990° were determined [39]. Its crystal lattice is dominated by short intermolecular C⋯H, H⋯H, H⋯Cl, S⋯Cl, C⋯C, and C⋯Cl contacts.

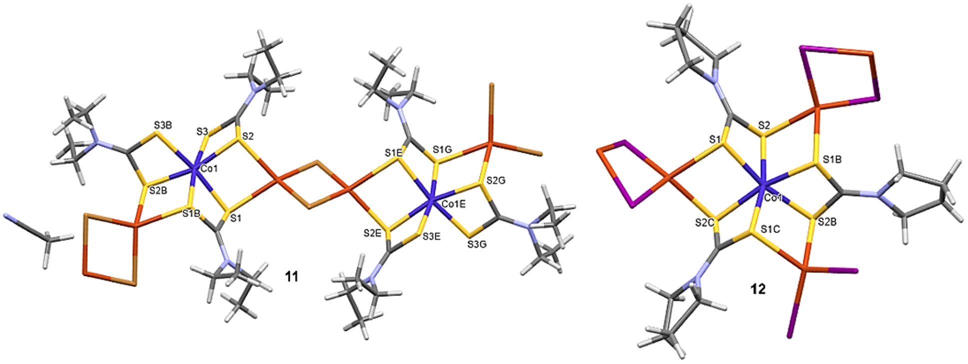

Figure 9. Molecular structures of complexes **11** and **12**.

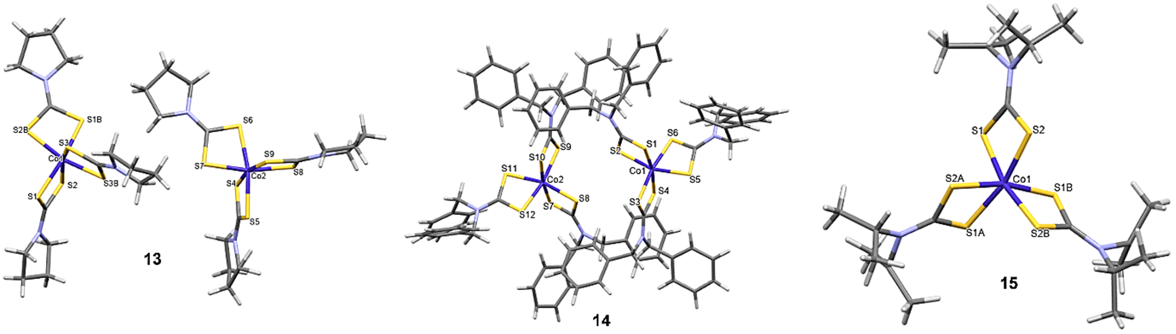

Figure 10. Molecular structure of complexes **13**, **14**, and **15**.

Cis-$[Co(dtc)_2(etpb)_2]BF_4$ (dtc = dimethyldithiocarbamaato ion $(CH_3)_2NCS_2^-$) and etpb = 4-ethyl-2,6,7-trioxa-1-phospha bicyclo[2.2.2] octane $(P(OCH_2)_3CC_2H_5))$ (**9**, Figure 8) crystallizes in the monoclinic *C*2/*c* space group [4]. Its central Co ion sits in a distorted octahedron that consists of a cis configuration arrangement of two etpb ligands. The mean distance of 2.171(1) Å for Co-P bonds resembles the 2.165(3) Å reported for trans-$[CoCl(dmgH)_2(pome)$, where dmgH = dimethylglyoximate ion and pome = trimethylphosphite $[P(OCH_3)_3]$ [4]. These distances are the shortest ever reported for Co-P bonds in Co(III)-phospine complexes. Other weaker and longer Co-P bonds include a mean value of 2.244(6) Å for trans-$[Co(NCS)_2(poet)_4]\cdot B(C_6H_5)_4$ [41], where poet = triethylphosphine $(P(OC_2H_5)_3)$, 2.222(2)-2.257(2) Å for trans-$[CoX(dmgH)_2(pome)]$ (X = CN^-, CH_2CN^-, CH_3^-, $CH_2CF_3^-$) [42] and 2.270(1) Å for trans-$[Co(i\text{-}C_3H_7)(dmgH)_2\{P(OCH_2)_3CCH_3\}]$ [42]. The Co-S bonds recorded a mean value of 2.284(2) Å for those trans to etpb and 2.267(1) Å for those trans to dtc. The Co-S_{mean} = 2.267(1) Å resembles those found in $Co(dtc)_3$ = 2.264(2) Å [43] and $[Co(dtc)(en)_2]^{2+}$ = 2.263(3) Å [4] (en = ethylenediammine). The elongation encountered by the Co-S bonds trans to etpb is connected to the small trans influence of etpb (0.017(2) Å) unlike the Co-N and Co-O bonds of the mixed-ligand Co(III)-phosphine complexes which gave a higher trans influence of 0.04-0.06 Å [44].

$[Co(pipdtc)(pome)_4](BF_4)_2$ (**10**, Figure 8), where pipdtc = piperidyldithiocarbamate cation with a seemingly disordered tetrafluoroborate anion, crystallizes in the monoclinic $P2_1/c$ space group [4]. Trans-effect/influence of P and S on the Co-P bonds was depicted as elongated 2.242(2) Å and 2.208(3) Å, respectively. The extended elongation of the Co-P bonds trans to P compared to S is connected to the extra mutual trans influence from some of the pome ligands. The mean distance for Co-S bonds is 2.288(3) Å. Interestingly, the study of complex **10** made Matsui *et al.* investigate further and come up with the conclusion that the trans-influences of phosphites, phosphornites, and phosphines on Co(III) ions are similar [4].

$[Co(dtc)_3]\cdot 2CuBr\cdot 2CH_3CN$ (dtc = *N, N*-dimethyl(dithio carbamato) (**11**, Figure 9) is a typical example of the 1:2 heterobimetallic adduct. It crystallizes in the monoclinic *C*2/*c* space group [45]. Its asymmetric unit is made up of a CuBr unit, a CH_3CN molecule, and one-half of the $Co(S_2(NEt_2)_3$ molecule that sits on a crystallographic two-fold axis. The CuBr unit is located in an inversion center for the dimeric planar Cu_2Br_2 that associates with two $[Co(S_2CNEt_2)_3]$ molecules of reversed chirality. The Co-S bond distances vary depending on the source of the sulfur atoms. For example, when S in Co-S is chelated to copper, the distance between Co and S is in the range 2.281(5)-2.292(4) Å, while for unchelated sulfur, the distance between the Co and S bonds is 2.245(5) Å. On the other hand, the range 2.265(1)-2.268(1) Å was obtained for Co-S bonds in the parent complex [45]. The acetonitrile solvate occupies voids left unfilled when the sulfur atoms are uncoordinated with CuBr. The crystal lattice of complex **11** is host to a number of short intermolecular interactions such as C···N, H···N, C···H, H···O, H···H, C···C, C···F, H···F, O···O, N···O and C···O contacts.

$[Co(dtc)_3]\cdot 3CuI$ (dtc = tetramethylene dithiocarbamato) (**12**, Figure 9) is a typical example of the 1:3 heterobimetallic adduct. It crystallizes in the *I*-43*d* space group of the cubic crystal system. Its asymmetric unit consists of one-third of $Co[(S_2CN(CH_2)_4]_3$ whose Co atom sits on a crystallographic three-fold axis. One-half of the Cu_2I_2 dimer sits on a crystallographic 2-fold axis, thus forming a polymeric bridge with the complex. Two independent Co-S distances of 2.259(1) and 2.304(5) Å were obtained despite having all sulfur atoms coordinated to the copper atom [45]. Table 3 shows the selected bond distances, angles, and solvents for crystal growth of complexes **1**-**12**. It shows the changes in bond angle and distances as the R substituents in the dithiocarbamate backbone changes or the ligand framework is replaced with a secondary ligand such as the P-ligand. Its crystal lattice consists of short intermolecular interactions such as H···S, Cu···Co, Cu···S, Cu···C, Cu···Cu and Cu···I contacts.

Table 3. Selected bond distances, angles, and crystal growth solvents for complexes **1-18**.

Complexes	Co-S (Å)	Co-P (Å) [a]	S-Co-S (°)	P-Co-P (°) [b]	Solvent(s) for crystal growth	Ref.
1	2.263(3)-2.270(3)		76.1(1)-76.5(1)		Benzene-ethanol (1:1)	[8]
2	2.262(3)		76.2(2)-166.5(2)		Acetone	[12]
3	2.2578(8)-2.2963(7)	2.2258(7)-2.2340(6)[a]	76.47(3)-167.84(3)	90.51(2)[b]	Diffusion of diethyl ether vapour into acetonitrile solution	[5]
4	2.269	2.276[a]	77.03-102.97	180[b]	Methanol-dichloromethane (2:1)	[5]
5	2.254(2)-2.273(2)		76.2(1)-167.2(1)		Acetone	[31]
6	2.253(1)-2.273(2)		76.24(5)-94.52(5)		Water-*N,N*-dimethylformamide	[20]
7	2.258(1)-2.292(1)		76.32(3)-167.65(4)		Ethanol	[32]
8	2.265(2)-2.304(1)	2.237(2)-2.242(2)[a]	75.95(7)-169.44(7)	87.01[b]	Chloroform	[39]
9	2.271(1)-2.278(2)	2.169(1)-2.172(1)[a]	76.00(5)-165.21(5)	92.51(5)[b]	Chloroform	[4]
10	2.282(3)-2.294(2)	2.199(2)-2.241(2)[a]	75.52 (7)	87.71(8)-170.80(8)[b]	Dichloromethane	[4]
11	2.281(5)-2.292(4)		76.4-92.9		Acetonitrile	[45]
12	2.259(1)-2.304(5)		76.3(2)-93.2(2)		Acetonitrile-dichloromethane	[45]
13	2.255(2)-2.284(3)		76.46(7)-96.36(7)		Slow diffusion of acetonitrile into dichloromethane solutions of complexes	[26]
14	2.251(4)-2.287(4)		76.3(1)-98.1(1)		Slow diffusion of acetonitrile into dichloromethane solutions of complexes	[26]
15	2.249-2.274		76.0-95.0		Slow diffusion of acetonitrile into dichloromethane solutions of complexes	[26]
16	2.352(2)-2.382(2)		71.1(1)-167.8(1)		Dichloromethane-ethanol	[48]
17	2.355(7)-2.379(7)		88.4(1)-114.5(1)		Chloroform-cyclohexane	[50]
18	2.365(2)-2.370(2)		93.31(8)-166.65(7)		Acetone	[52]

Tris(pyrrolidine-1-carbodithioato)cobalt (III) of the formula $[Co(S_2CN(CH_2)_4)_3]$ (**13**, Figure 10) crystallizes in the *C*2/*c* space group of the monoclinic crystal system [26]. Its asymmetric unit consists of two molecules of complex **13** and the ligand of one of the molecules is located on a crystallographic 2-fold axis. The geometrical alignments of the two molecules are not significantly different except for their Co-S bond distances, which show a considerable long-range stretch of 2.254(3)-2.291(2) Å. Such stretches have been observed in heterobimetallic adducts; $[Co(S_2CN(CH_2)_4)_3]\cdot 3CuI$ [45], $[Co(S_2CN(CH_2)_4)_3]\cdot CuBr$ [46], and $[Co(S_2CN(CH_2)_4)_3]\cdot 3CuBr\cdot MeCN$ [47] with ranges 2.259(1)-2.304(5), 2.258(2)-2.307(2) and 2.26(1)-2.30(1) Å, respectively. The stretch phenomenon has also been observed in the dihydrogen complex $[Co(S_2CNH_2)_3]$ [32]. The striking variation in the Co-S bond distances is attached to the rigid pyrrolidine ligands, which enforce a level of restriction on the number of adaptable conformations so that the molecule can retain a stable geometry. Its crystal lattice is dominated by short H⋯S and H⋯H contacts from hydrogen-bond interactions in the range 2.816-2.850 Å and 2.343 Å, respectively.

Tris(*N, N*-dibenzyldithiocarbamato)cobalt(III) of the formula $[Co(S_2CN(CH_2Ph)_2)_3]$ (**14**, Figure 10) crystallizes in the non-centrosymmetric *P*2/1 space group with two molecules of opposite chirality in the asymmetric unit [26]. It is isostructural with a $[Fe^{III}(S_2CN(CH_2Ph)_2)_3]$ crystalline analogue [15]. The Co-S distances in the two molecules spread out in the range 2.250(3)-2.283(4) Å to form an average value of 2.26 Å. The deviations of the Co atoms from the S_2CN planes are 0.420, 0.214, 0.428, 0.422, 0.331 and 0.263 Å. The phenyl rings are closely normal to the S_2CN plane with angles 59.4-87.7° in molecule **1** and 66.4-87.7° in molecule **2**. The crystal lattice of complex **14** is dominated by short intermolecular H⋯H, C⋯H, and H⋯S contacts.

Tris(*N, N*-diisopropyldithiocarbamato)cobalt(III) of the formula $[Co(S2CNPr^i{}_2)_3$ (**15**, Figure 10) crystallizes in the rhombohedral *R*3*c* space group [26]. The molecule lies on a crystallographic 3-fold axis such that the asymmetric unit consists of just one ligand framework. The precision of its determination was vehemently affected by the high temperature (295 K) of the measurement, resulting in a high thermal motion disorder. Deviations of 0.09 and -0.14 Å were experienced by C2 and C5, respectively, while the Co atom deviated by 0.17 Å from the S_2CN plane. A difference of 0.02 Å was observed for the two independent Co-S bond distances whose average equals 2.26 Å. The high-temperature determination prevented satisfactory resolution of the components of the non-hydrogen atoms. The pyramidal geometry expected of the central carbon atom of the isopropyl groups is not adequately defined. It was observed that the influence of substituents (aliphatic hydrocarbons) on sulfur atoms through the ligand field strength is not through the predicted π-bonding of the S_2CN moiety but through intra-ligand S⋯H-C interactions whose strength rises with increase in the bulkiness of the substituents. Table 3 shows the selected bond distances, angles, and solvents for crystal growth in complexes **1**-**18**. It shows the changes in bond angles and distance as the R substituents in the dithiocarbamate backbones are changed or modified.

2.2. Rh(III) complexes

Dichloromethane-solvated tris-(morpholinocarbodithiato) rhodium(III) (**16**, Figure 11) that crystallizes in the *P*-1 space group of the triclinic crystal system is isostructural with the chromium(III) and manganese(III) congeners and isomorphous with the cobalt(III) analogue [48]. Its molecular structure possesses stereoscopic pairs in its molecular packing in the unit cell. These peculiarities are present in the Mn(III), Cr(III), and Co(III) analogues.

Each molecule of the dichloromethane solvate approaches the complex by inclusion. The crystal lattice of complex **16** is made up of well-separated metal complexes that have solvate molecules fitted into crystallographic holes. Its MS_6 coordination core is a trigonally distorted octahedron with symmetrical spherical ground states. The Mn(III) analogue is an exception in this respect, with significant deviations from the MS_6 model with uneven Mn-S bond distances that are attributed to Jahn-Teller-driven tetragonal distortion. Typically, the mean M-S bond distances increase down the group for Co and Rh metals with d^6 configuration; Co-S = 2.275 Å and Rh-S = 2.369 Å. Furthermore, there is an increase in the M-S distances of Cr, Mn, and Fe as the unpaired electron occupancy in the d-shell increases; Cr-S (d^3) = 2.406 Å, Mn-S (d^4) = 2.461 Å and Fe-S (d^5) = 2.430 Å. The "bite" angle S-M-S of the ligand shares a strong correlation with the M-S bond distances independent of factors such as trigonal distortion, tetragonal distortion, or packing effects [49]. Its crystal lattice hosts short H⋯Cl, H⋯S, and H⋯O intermolecular hydrogen bond interactions.

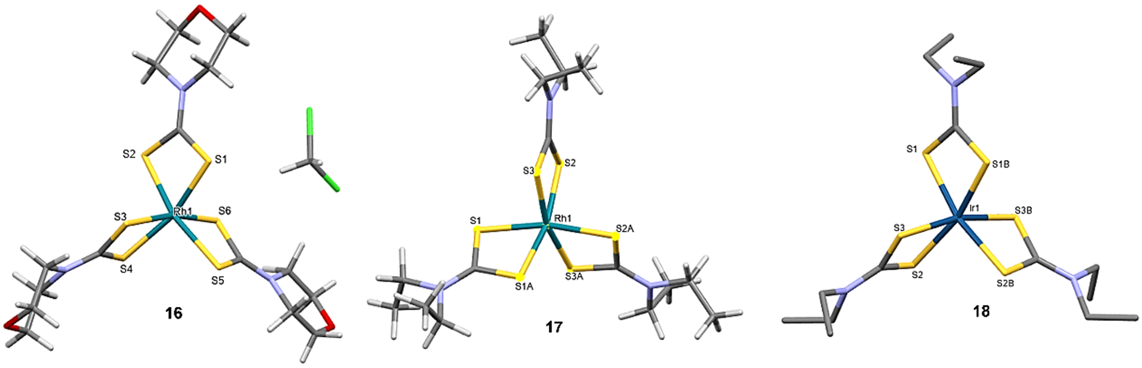

Figure 11. Molecular structure of complexes **16**-**18**.

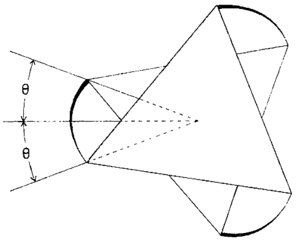

Figure 12. The IrS_6 coordination polyhedron as projected on a 3-fold axis [52].

Tris(diethyldithiocarbamato)rhodium(III) (**17**, Figure 11) crystallizes in the monoclinic $P2_1/a$ space group with $Z = 4$ in the unit cell. Its unit cell dimensions are similar to those reported for Mn and As derivatives. The solved structure of compound **17** did not show distortion of the RhS_6 core, while the As and Mn derivatives showed varying large distortions about their MS_6 cores. Interestingly, $[Rh(CS_2NEt_2)_3]$ and $[As(CS_2NEt_2)_3]$ have previously been determined [50]. Its lattices contain discrete molecules of $[Rh(CS_2NEt_2)_3]$. Despite being isomorphous with the As(III) and Mn(III) analogues, they are still quite different geometrically and from the perspective of their crystal packing. The Rh atom is distortedly hexa-coordinated to three quasibidentate ligands whose S_2CNC_2 fragments are planar and lie parallel to the faces of the unit cell. Complex **17** is different from other [M(dtc)$_3$] systems whose overall molecular symmetries align well with the D_3 approximation. The terminal methyl groups on the ligand lie on alternate sides of the ligand plane without symmetry. Two ligands give the bladed propeller configuration, whereas the third ligand is the mirror image of the configuration. The flexibility of the solid-state packing effect is reflected in the strong possibility of free rotation about the ethyl-nitrogen bonds. There is also a crystal-clear distortion from the ideal D_3 symmetry as revealed by the asymmetrical Rh-S bond distances and ligand bite angles around the Rh centre; although the Rh-S distances do not deviate from the mean value of 2.36(8) Å. Table 3 shows the selected bond distances, angles, and solvent for crystal growth in complexes **16** and **17**. It shows the changes in bond angles and distance as the R substituents in the dithiocarbamate backbones are changed or modified. Unfortunately, hydrogen atoms were missing from the refinement of the crystal structure of complex **17**. Hence, its lattice lacks intramolecular and intermolecular short contacts and hydrogen-bond interactions. Interestingly, the redetermined polymorph (refcode: TEDCRH01) [51] of complex **17** was reported almost 24 years later as a crystal in the space group $C2/c$. A comparison of its molecular structure with that of complex **17** revealed some fascinating trends. For example, the distances of the Rh-S bonds of 2.351 and 2.353 Å reveal the symmetrical nature of TEDCRH01 compared to the unsymmetrical nature of the Rh-S bonds (2.360. 2.363, 2.3552, 2.378, 2.3601, and 2.369 Å) in complex **17**. Likewise, the symmetrical nature of TEDCRH01 is reflected by their C-S bonds of lengths 1.712, 1.712, 1.709(6), 1.704(6), 1.704(6) and 1.709(6) Å and C-N bonds of lengths 1.33, 1.330(6) and 1.330(6) Å compared to the unsymmetrical 1.692, 1.7279, 1.728, 1.7303, 1.707 and 1.683 Å for C-S and 1.3795, 1.323 and 1.357 Å recorded for C-N bonds. In terms of the S-Rh-S bond angles, TEDCRH01 shows slightly symmetrical bites of 73.70, 74.11, and 73.70° compared to the unsymmetrical 73.57, 73.62 and 73.43° recorded for complex **17**. The two complexes share similar properties related to symmetry, such as the two-fold screw axis. On the other hand, complex **17** has an inversion center at [0,0,0] and a glide plane that is perpendicular to the [0,1,0] axis with a glide component [½,0,0]. TEDCRH01 differs considerably from complex **17** by virtue of its 2-fold rotation axis, centering vector, inversion centre at [¼,¼,0], a glide plane perpendicular to the [1,1,0] axis with a glide component [0,0,½] and another glide plane that is perpendicular to [0,1,0] with a glide component [½,0,½]. Its crystal lattice is dominated by hydrogen-bond interactions with H⋯S contacts of distances 2.989, 2.989, 2.366, 2.366, 2.947 and 2.947 Å resulting in a crystalline 2D aggregate.

2.3. Ir(III) complexes

Tris(diethyl(dithiocarbamato)iridium(III) (**18**, Figure 11) [52], which is isostructural with its cobalt(III) analogue [8,33], crystallizes in the $C2/c$ space group of the monoclinic crystal system with the structural formula $[Ir(S_2CNEt_2)_3]$. Its unit cell is made up of discrete molecules seated on a 2-fold symmetry that passes through (i) the axis of one of the ligands and (ii) the metal atom. The other ligand has a slightly distorted S_2CNC_2 plane, as well as an iridium center, whose deviation from the plane is small but significant. The mean Ir-S bond distance of 2.36(7) Å in compound **18** is reasonably consistent with what was reported for $[Ir_2(C_7H_7S_2)_3(CO)_2(PPh_3)_2]$ [52]. Just as in other metal complexes of the form $[M(S_2NEt_2)_3]$ where M = Co [8,33], Fe [53], Cr [52], Ru [54], the electronic distortion mechanism is inherently absent resulting in the MS_6 geometry (Figure 12) that is approximately equivalent to D_3 with a structural moiety that depends on the metal-sulphur distance. The geometrical alignments in Complex **18** have been considered 'anomalous', as they should clearly have crystallized in the $P2_1/c$ space group rather than $C2/c$. The possibility of a wrong assignment of $C2/c$ was dismissed after a series of long exposures to Weissenberg photographs. Table 3 shows the selected bond distances, angles, and solvents for crystal growth in complex **18**. It shows the changes in bond angles and distance as the R substituents in the dithiocarbamate backbones are changed or modified.

3. Conclusions and future perspectives

The solid-state crystal and molecular description of single and mixed ligand dithiocarbamate complexes of cobalt, rhodium, and iridium in the +3 oxidation states are presented herewith their wide arrays of chelating and bridging modes ranging from monomeric, dimeric, and polymeric networks to 3D supramolecular aggregates. The diversity in their coordination modes is connected to the steric profile of the carbamate N substituents on the dithiocarbamate ligands and the trans effects of P-ligands other than dithiocarbamate, pointing out the importance of modifying the ligand backbones and coordination spheres (primary and secondary) with the aim of generating different structural platforms. The continuous determination of geometrical alignments and structural types in dithiocarbamates and their derivatives no doubt increased their utility in the fields of chemistry, biology, medicine, and material science.

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CRediT authorship contribution statement

Conceptualization: Ibukun Oluwaseun Shotonwa; Methodology: Ibukun Oluwaseun Shotonwa; Software: Ibukun Oluwaseun Shotonwa; Validation: Ibukun Oluwaseun Shotonwa; Formal Analysis: Ibukun Oluwaseun Shotonwa, Adebayo Ponle Oduwole, Oluwapelumi Martin Agosu, Abosede Funke Yusuf, Simeon Okechukwu Eze; Investigation: Ibukun Oluwaseun Shotonwa; Resources: Adebayo Ponle Oduwole, Oluwapelumi Martin Agosu, Abosede Funke Yusuf, Simeon Okechukwu Eze; Data Curation: Ibukun Oluwaseun Shotonwa; Writing - Original Draft: Ibukun Oluwaseun Shotonwa; Writing - Review and Editing: Ibukun Oluwaseun Shotonwa, Adebayo Ponle Oduwole, Oluwapelumi Martin Agosu, Abosede Funke Yusuf, Simeon Okechukwu Eze; Visualization: Adebayo Ponle Oduwole, Oluwapelumi Martin Agosu, Abosede Funke Yusuf, Simeon Okechukwu Eze; Funding acquisition: Ibukun Oluwaseun Shotonwa; Supervision: Ibukun Oluwaseun Shotonwa; Project Administration: Ibukun Oluwaseun Shotonwa.

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