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Functionalised dithiocarbamate complexes: Synthesis and molecular structures of 2-diethylaminoethyl and 3-dimethylaminopropyl dithiocarbamate complexes \([\text{M}\{\text{S}_2\text{CN(CH}_2\text{CH}_2\text{NEt}_2\}_2\}_n]\) and \([\text{M}\{\text{S}_2\text{CN(CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\}_2\}_n]\) (\(n = 2, M = \text{Ni, Cu, Zn, Pd}\); \(n = 3, M = \text{Co}\))


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Functionalised dithiocarbamate complexes: Synthesis and molecular structures of 2-diethylaminoethyl and 3-dimethylaminopropyl dithiocarbamate complexes \([M\{S_2CN(CH_2CH_2NEt_2)\}_2]\) and \([M\{S_2CN(CH_2CH_2CH_2NMe_2)\}_2]\) (n = 2, M = Ni, Cu, Zn, Pd; n = 3, M = Co)

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Abstract

The amine-functionalised dithiocarbamate salts K[S\(_2\)CN(CH\(_2\)CH\(_2\)NEt\(_2\))] and K[S\(_2\)CN(CH\(_2\)CH\(_2\)CH\(_2\)NMe\(_2\))] have been prepared and used for the synthesis of a number of bis and tris-dithiocarbamate complexes. The molecular structures of five of these namely, \([M\{S_2CN(CH_2CH_2NEt_2)\}_2]\) (M = Cu, Ni), \([M\{S_2CN(CH_2CH_2CH_2NMe_2)\}_2]\) (M = Cu, Pd) and \([Co\{S_2CN(CH_2CH_2CH_2NMe_2)\}_3]\), have been elucidated by X-ray crystallography.

Keywords: dithiocarbamate, crystal structures, amine, functionalised

Introduction – Dithiocarbamates are versatile ligands capable of forming complexes with most of the elements and able to stabilise transition metals in a variety of oxidation states [1]. They have a diverse range of applications, for example, they are widely used in inorganic analysis, can be used to separate different metal ions by
HPLC and capillary gas chromatography and find use as rubber vulcanization accelerators, fungicides and pesticides [1]. A developing interest in dithiocarbamate chemistry is the functionalisation of the dithiocarbamate substituents which allows more complex architectures to be developed and potentially gives rise to tuneable physical properties [2-10]. One common backbone functionalisation is the 2-hydroxyethyl group which confers some degree of water solubility to its complexes [11-16] and we recently reported the synthesis of complexes containing the related 2-methoxyethyl functionalised dithiocarbamate ligand [17]. In both of these, however, the pendant oxygen atoms are not easily further functionalised. In contrast, related secondary amine-functionalised dithiocarbamates should be amenable to later elaboration via addition of electrophiles to the nitrogen lone-pair. A survey of the literature shows that reports of complexes of this type are extremely limited [18-20]. In the late 1960s, McCormick and co-workers reported the synthesis of a number of 2-diethylaminoethyl dithiocarbamate complexes and showed that they could be readily protonated upon addition of gaseous HCl [18-19]. There appears to have been very little further work in this area for almost 40 years, the only other report of a 2-diethylaminoethyl dithiocarbamate complex being that of \([Au(SCN)_{2}\{S_{2}CN(CH_{2}CH_{2}NEt_{2})_{2}\}]\) in the early 1980s [20]. This is proposed to have a double linkage isomer in which one isocyanate is metal bound, while the second ligand is bound via all three nitrogen atoms, although this seems unlikely.

As part of our continued interest [2,3,17] in the synthesis and applications of functionalised-dithiocarbamate complexes we wanted to develop the chemistry of amine-functionalised ligands with a view to utilising these in applications ranging from dithiocarbamate-stabilised gold nanoparticles [10,21] to building–blocks for star-shaped polymers via reversible addition-fragmentation transfer (RAFT) polymerisation [22-23]. Herein we report our initial studies in this area in which we focus on a re-investigation of aspects of the chemistry of the 2-diethylaminoethyl dithiocarbamate ligand and the development of related 3-dimethylaminopropyldithiocarbamate chemistry.

**Results and discussion** - Potassium(2-diethylaminoethyl) [18] and potassium(3-dimethylaminopropyl) dithiocarbamates were readily prepared in methanol upon addition of carbon disulfide to a basic solution of the commercially available
secondary amines, HN(CH₂CH₂NEt₂)₂ and HN(CH₂CH₂CH₂NMe₂)₂ respectively. No attempt was made to isolate either of these salts, rather they were used as generated, addition of the metal(II) acetates (M = Ni, Cu, Zn) or sodium tetrachloropalladate. The 2-diethylaminoethyldithiocarbamate complexes \([M\{S₂CN(CH₂CH₂NEt₂)₂\}_2]\) (1-4) precipitated from solution and were isolated after filtration and washing with methanol and water. The corresponding 3-dimethylaminopropyl-dithiocarbamate complexes \([M\{S₂CN(CH₂CH₂CH₂NMe₂)₂\}_2]\) (5-8) displayed some solubility in methanol and were best isolated upon initial extraction of the complexes into dichloromethane.

All were isolated as solids in good to high yields. The zinc complexes were somewhat sticky and all attempts to recrystallise them failed. This is possibly due to the secondary coordination of one or more of the amine-substituents to the zinc centre since zinc bis(dithiocarbamate) complexes are well-known to form both five and six-coordinate adducts with amines [1]. Indeed in related work, O’Brien and co-workers have prepared and crystallographically characterised 3-dimethylaminopropyl-methyl dithiocarbamate complexes [24-26] including the zinc complex, \([Zn\{S₂CN(Me)CH₂CH₂CH₂NMe₂\}_2]\) [24] which is shown to be polymeric in the solid state, molecular sub-units being linked via secondary zinc-nitrogen interactions.
Characterisation of 1-8 was relatively straightforward. All showed the expected absorptions in the IR spectra associated with the dithiocarbamate ligands. The nickel, zinc and palladium complexes were diamagnetic as expected, and $^1$H and $^{13}$C NMR spectra proved characteristic. In the latter all showed a single low-field resonance associated with the backbone carbon of the dithiocarbamate at ca. 210 – 200 ppm. Proton NMR spectra were characteristic of each ligand type. Thus 2-diethylaminoethylthiocarbamate complexes showed two relatively low-field triplets associated with the two-carbon backbone, and a quartet and triplet at slightly higher field assigned to the ethyl substituents. The 3-dimethylaminopropylthiocarbamate complexes each displayed three equal intensity signals associated with the methylene groups; that bound to nitrogen appearing at relatively low-field and the central one appearing as a multiplet, together with a sharp singlet assigned to the methyl groups. Elemental analyses were consistent with the proposed formulations.

While we were unable to recrystallise either of the zinc complexes, good quality crystals of all other complexes were obtained upon slow diffusion of either methanol (2-diethylaminoethyl) or hexanes (3-diethylaminopropyl) into saturated dichloromethane solutions. The crystal structures of four of these, namely [Ni$\{S_2CN(CH_2CH_2NEt_2)\}_2$] (1), [Cu$\{S_2CN(CH_2CH_2NEt_2)\}_2$] (2), [Cu$\{S_2CN(CH_2CH_2CH_2NMe_2)\}_2$] (6) and [Pd$\{S_2CN(CH_2CH_2CH_2NMe_2)\}_2$] (8), were carried out the results of which are summarised in Figures 1-4 and Table 1. Complexes 1 and 2 are isostructural (P 1bar) with the metal atom lying on the inversion centre. Complexes 6 and 8 are also isostructural (P2$_1$/n), do not have molecular symmetry, and hence contain two inequivalent dithiocarbamate ligands. A unit cell was also collected for [Ni$\{S_2CN(CH_2CH_2CH_2NMe_2)\}_2$] (5) which was isostructural with 6 and 8 and full data was not collected.
In all four complexes the metal adopts the expected square-planar coordination geometry and simple monomeric complexes are seen with no significant intermolecular interactions involving the metal atom been found in any case. This is not surprising for the nickel and palladium complexes as group 10 bis(dithiocarbamate) complexes are known to crystallise in this manner [1]. More notably, copper(II) bis(dithiocarbamate) complexes adopt two distinct geometries in the solid state consisting of either isolated monomeric units or dimeric structures held together by intermolecular copper-sulfur interactions, the latter leading to a substantial deviation from planarity of the CuS₄ moiety. Both 2 and 6 fall into the first category which is relatively uncommon and generally associated with bulky substituents [1], although we recently found that the related complex [Cu(S₂CN(CH₂CH₂OMe)₂] [17] also contains isolated monomeric subunits with no significant intermolecular interactions. The backbone substituents on the 2-diethylaminoethylthio carbamate complexes 1 and 2 adopt the expected “up-down” arrangement, while in contrast for both 3-dimethylaminopropylthio carbamate complexes 6 and 8 one dithiocarbamate ligand adopts an “up-up” configuration. We have previously noted that this conformation is associated with significant intermolecular interactions [27]. In both 6 and 8 while there are no significant intermolecular interactions involving the metal centres, a range of short H…H, C…H and S…H intermolecular interactions are noted and these may account for the observed relative arrangement of the dithiocarbamate substituents. All bond lengths and angles are within generally accepted ranges [1] and the only significant point of note is the relative asymmetry of the copper-sulfur interactions in 2 as compared to those in 6.

Reaction of cobalt acetate with both K[S₂CN(CH₂CH₂NEt₂)₂] and K[S₂CN(CH₂CH₂CH₂NMe₂)₂] resulted in the formation of [Co(S₂CN(CH₂CH₂NEt₂)₃] (9) and [Co(S₂CN(CH₂CH₂CH₂NMe₂)₂]₃ (10) respectively. The former was always oily and we were unable to obtain satisfactory elemental analysis data but its formation was easily confirmed by NMR spectroscopy. Both showed good solubility in hexanes and slow evaporation of a concentrated hexane solution of 10 resulted in the isolation of a crystalline product. The results of the single crystal X-ray structure are summarised in Figure 5 and Table 1. All hydrogen atoms were located from Fourier difference maps and their coordinates and
isotropic thermal parameter were freely refined. The complex crystallises in the monoclinic space group C\textsubscript{2}/c. The crystallographically imposed two-fold symmetry leads to two crystallographically different dithiocarbamate ligands, and the overall coordination geometry at cobalt atom is approximately octahedral. Bond lengths and angles within the different dithiocarbamate ligands are (within experimental error) the same and the deviation from the octahedral coordination environment is imposed by the small bite-angles subtended at the metal centre.

NMR data for both are in accord with the proposed structures, the diastereotopic nature of the methylene protons resulting in two well-separated multiplets for the protons closest to the dithiocarbamate functionality.

Conclusions – We have shown in this work that, despite the paucity of examples of amine-functionalised dithiocarbamate ligands and their complexes [2,3,18-20,24-26], these can be easily prepared and characterised. In general, 3-dimethylaminopropyl-dithiocarbamate complexes are easier to purify and handle than their 2-diethylaminoethyl-dithiocarbamate counterparts. All show good solubility in a range of organic solvents with most being highly soluble in hexanes. In future work we aim to generate analogous quaternary ammonium salts with the expectation that they will show good water solubility. We believe that this control over the organic-water solubility of dithiocarbamate complexes may have useful consequences in their behaviour in a range of different applications especially in the medicinal area.
Experimental

General methods - All reactions were carried out in air using standard bench reagents. NMR spectra were run on a Bruker AMX400 spectrometer and referenced internally to the residual solvent peak ($^1$H and $^{13}$C). Infrared spectra were run on a Nicolet 205 FT-IR spectrophotometer as KBr discs. Fast atom bombardment mass spectra were recorded on a VG ZAB-SE high resolution mass spectrometer and elemental analyses were performed in house. HN(CH$_2$CH$_2$NEt)$_2$ and HN(CH$_2$CH$_2$CH$_2$NMe)$_2$ were purchased from Aldrich and used without further purification.

X-ray data collection and solution - Single crystals were mounted on glass fibres and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K. Data reduction was carried out with SINT PLUS [28] and absorption correction applied using the programme SADABS [29]. Structures were solved by direct-methods [30] and developed [31] using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic displacement parameters. For [{Co(S$_2$CN(CH$_2$CH$_2$CH$_2$NMe)$_2$)$_3$}] hydrogens were located from difference maps and refined isotropically, while for all other complexes they were placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package [32]. CCDC reference numbers 687328 - 687332.

Preparation of K[S$_2$CN(CH$_2$CH$_2$NEt)$_2$] - HN(CH$_2$CH$_2$NEt)$_2$ (0.74 g, 3.40 mmol) was added to MeOH (30 ml) and KOH (0.2 g, 3.5 mmol). The solution was left to stir for 5 mins and CS$_2$ (0.26 g, 3.4 mmol) was added drop-wise and left to stir for 1 h. This produced a pale-yellow solution which was used for all further experiments.

Preparation of K[S$_2$CN(CH$_2$CH$_2$CH$_2$NMe)$_2$] - HN(CH$_2$CH$_2$CH$_2$NMe)$_2$ (0.75 g, 4.00 mmol) was added to water (30 ml) and KOH (0.2 g, 3.6 mmol). The solution was left to stir for 5 mins and CS$_2$ (0.36 g, 4.7 mmol) was added drop-wise and left to stir for 1 h. This produced a pale-yellow solution which was used for all further experiments.

Preparation of [M(S$_2$CN(CH$_2$CH$_2$NEt)$_2$)$_n$](n = 2, M = Ni, Cu, Zn, Pd; n = 3, M =
Nickel acetate (0.42 g, 1.7 mmol) was added to a methanol solution of K[S₂CN(CH₂CH₂NEt₂)₂] and the mixture stirred for 1 h producing a dark green precipitate. The green solid was isolated by filtration and washed with MeOH (2 x 5 ml) and water (3 x 10 ml). Recrystallisation upon slow mixing of methanol with a concentrated dichloromethane solution gave green needles. Yield (0.89 g, 89 %).

**¹H NMR(CDCl₃):** δ 3.59 (t, 8 H, J 6.4, S₂CNCH₂CH₂), 2.59 (t, 8 H, J 6.4, CH₂NEt₂), 2.45 (q, 16 H, J 6.8, CH₃CH₃), 0.94 (t, 24 H, J 6.9, CH₃CH₂).

**¹³C NMR(CDCl₃):** 206.8, 49.9, 48.9, 47.5, 12.0.

**IR  v/cm⁻¹:** 2966(m), 2931(w), 2798(m), 1514(s), 1463(w), 1429(m), 1382(m), 1350(m), 1296(m), 1278(m), 1240(m), 1182(s), 1145(w), 1128(w), 1083(w), 1068(m), 981(m), 954(w), 904(w), 850(w), 788(w), 758(m), 665(m), 626(w), 590(w), 532(w), 453(w).

**MS: m/z:** 154 (100%), 259 (42%), 308 (50%), 440 (20%), 639 (M⁺, 78%).

**Elemental analysis found (calc. for C₂₆H₅₆S₄N₆Ni₁):** C: 48.45 (48.83), H: 8.87 (8.76), N: 12.93 (13.14).

**Crystal Data:** Green needle-like crystals, size 0.13 × 0.08 × 0.04 mm, triclinic, space group P1bar, a = 7.0542(8) Å, b = 10.5479(12) Å, c = 12.8979(15) Å, α = 71.564(2)°, β = 75.658(2)°, γ = 74.035(2)°, V = 861.63(17) Å³, Z = 1, d calc = 1.233 g/cm³, µ = 0.830 mm⁻¹, F(000) = 346, final R indices [F²>2σ] R₁ = 0.032, wR₂ = 0.079 R indices (all data) R₁ = 0.036, wR₂ = 0.082.

[Cu[S₂CN(CH₂CH₂NEt₂)₂]₂] – from copper acetate - large brown crystals - yield (0.94 g, 78 %).

**IR  v/cm⁻¹:** 2968(m), 2933(w), 2796(m), 1508(s), 1463(w), 1429(m), 1384(m), 1297(m), 1268(m), 1240(m), 1182 (m), 1143(w), 1128(w), 1068(m), 981(m), 952(w), 788(w), 628(w).

**MS: (APCI+):** m/z 645, (M⁺ 100%).

**Elemental analysis found (calc. for C₂₆H₅₆S₄N₆Cu₁):** C: 48.36 (48.45), H: 8.87 (8.76), N: 12.24 (13.04).

**Crystal data:** Brown crystals, size 0.32 × 0.16 × 0.16 mm, triclinic, space group P1bar, a = 7.0626(8) Å, b = 10.568(1) Å, c = 12.8979(2) Å, α = 71.284(2)°, β = 75.247(2)°, γ = 73.866(2)°, V = 865.28(17) Å³, Z = 1, d calc = 1.237 g/cm³, µ = 0.897 mm⁻¹, F(000) = 347, final R indices [F²>2σ] R₁ = 0.029, wR₂ = 0.077 R indices (all data) R₁ = 0.031, wR₂ = 0.078.

[Zn[S₂CN(CH₂CH₂NEt₂)₂]₂] – from zinc acetate - white solid - yield (0.97 g, 72 %).

**¹H NMR:** δ 3.90 (t, 8 H, J 7.3, S₂CNCH₂CH₂), 2.80 (t, 8 H, J 7.3, CH₂NEt₂), 2.54 (q, 16 H, J 7.1 CH₃CH₃), 1.02 (t, 24 H, J 7.1, CH₃CH₂).

**¹³C NMR:** δ 203.5, 54.2, 49.4,
47.5, 12.0. IR ν/cm⁻¹: 2968(w), 2933(w), 2844(w), 2871(w), 1550(w), 1481(s), 1444(w), 1419(m), 1382(m), 1348(w), 1288(w), 1272(w), 1240(w), 1213(m), 1145(w), 1136(w), 1070(m), 991(s), 777(w), 758(m), 611(m), 522(w), 478(w).

Elemental analysis found (calc. for C26H56S4N6Zn1.CH2Cl2) %: C: 44.38 (44.63), H: 7.94 (7.99), N: 11.50 (11.57).

[Co{S2CN(CH2CH2CH2NEt2)2}]3 - from cobalt acetate – oily green solid - yield (0.68 g, 36 %). ¹H NMR: δ 3.86 (m, 6 H, J ca. 6.9), 3.67 (m, 6 H, J ca. 6.9), 2.55 (t, 12 H, J 7.0), 1.04 (t, 36 H, J 7.1). MS: m/z 154 (100%), 213 (6%), 258 (10%), 307 (21%), 639 (32%), 931 (M⁺, 22%).

Preparation of [M{S2CN(CH2CH2CH2NMe2)2}]n (n = 2, M = Ni, Cu, Zn, Pd; n = 3, M = Co) - Nickel acetate (0.49 g, 2.1 mmol) was added to a methanol solution of K[S2CN(CH2CH2CH2NMe2)2] and the mixture stirred for 1 h producing a green solution with some precipitate. The solvent was removed on the rotary evaporator and the residue dissolved in CH2Cl2 (25 ml), washed with water (3x10 ml), and dried over anhydrous magnesium sulphate for 30 mins. The solid was obtained by removal of solvent on the rotary evaporator and dried in vacuo. The product was recrystallised from the slow mixing of hexane into a saturated dichloromethane solution. Yield (0.87 g, 77 %). ¹H NMR: δ 3.58 (t, 8 H, J 7.6, S2CNCH2), 2.25 (t, 8 H, J 6.9, CH2NMe2), 2.18 (s, 24 H, NCH3), 1.79 (t, 8 H, J 7.5, CH2CH2CH2). ¹³C NMR: δ 206.7, 56.4, 47.7, 45.3, 25.1. IR ν/cm⁻¹: 2939(w), 2856(w), 2813(w), 2761(w), 2717(w), 1506(s), 1444(m), 1371(m), 1299(m), 1232(m), 1209(w), 1178(m), 1155(m), 1126(m), 1099(m), 1068(m), 1041(m), 958(m), 931(w), 881(w), 819(m), 758(m),
742(w), 648(w), 628(w), 462(w), 412(w). MS: m/z 154 (100%), 307 (31%), 460 (6%), 583 (M⁺ 10%). Elemental analysis found (calc. for C₂₂H₄₈S₄N₆Ni): C: 45.09 (45.28), H: 8.37 (8.29), N: 14.12 (14.40).

\[ Cu(S₂CN(CH₂CH₂CH₂NMe₂)₂)₂ \] – from copper acetate - large brown crystals - yield (0.72 g, 62%). IR ν/cm⁻¹: 2939(w), 2856(w), 2813(w), 2759(w), 2717(w), 1502(s), 1460(m), 1431(w), 1315(w), 1299(m), 1242(w), 1230(m), 1176(m), 1155(m), 1128(m), 1099(m), 1068(w), 1041(m), 978(w), 960(m), 879(w), 819(m), 742(m), 643(w), 623(w), 466(w). MS: (APCI+) m/z, 214 (32%), 230 (25%), 246 (32%), 248 (59%), 250 (100%), 294 (34%), 587 (M⁺ 16%). Elemental analysis found (calc. for C₂₂H₄₈S₄N₆Cu): C: 41.81 (41.04), H: 7.93 (7.43), N: 13.07 (12.49).

Crystal data: Brown crystals, size 0.42 × 0.36 × 0.22 mm, monoclinic, space group P2₁/n, a = 17.1614(16) Å, b = 8.6011(8) Å, c = 21.597(2) Å, β = 109.8910(10)°, V = 2997.7(5) Å³, Z = 4, d_calc = 1.304 g/cm³, μ = 1.029 mm⁻¹, F(000) = 1260, final R indices [F²>2s] R₁ = 0.028, wR₂ = 0.074, R indices (all data) R₁ = 0.031, wR₂ = 0.075.

\[ Zn(S₂CN(CH₂CH₂CH₂NMe₂)₂)₂ \] – from zinc acetate – sticky white solid - yield (0.69 g, 58%). ¹H NMR: δ 3.83 (t, 8 H, J 7.6, S₂CNCH₂), 2.37 (t, 8 H, J 7.1, CH₄NMe₂), 2.3 (s, 24 H, NCH₃), 1.97 (m, 8 H, J 5.9 CH₂CH₂CH₂). ¹³C NMR: δ 204.2, 56.8, 53.1, 45.5, 24.7. IR ν/cm⁻¹: 2968(w), 2940(w), 2856(w), 2813(w), 2782(w), 2760(w), 2716(w), 1500(s), 1444(w), 1372(m), 1314(m), 1299(m), 1259(w), 1247(w), 1230(m), 1208(w), 1176(m), 1154(m), 1099(w), 967(w), 978(w), 960(m), 819(m), 758(w), 629(w). MS: m/z 154 (100%), 307 (29%), 589 (9%). Elemental analysis found (calc. for C₂₂H₄₈S₄N₆Zn): C: 37.05 (37.92), H: 6.81 (6.85), N: 10.45 (11.06).

\[ Pd(S₂CN(CH₂CH₂CH₂NMe₂)₂)₂ \] – from Na₂PdCl₄ – yellow solid - yield (0.38 g, 92%). ¹H NMR: δ 3.69 (t, 8 H, J 7.5, S₂CNCH₂), 2.30 (t, 8 H, J 6.9, CH₂NMe₂), 2.19 (s, 24 H, NCH₃), 1.84 (m, 8 H, J 7.5, CH₂CH₂CH₂). ¹³C NMR: δ 210.3, 56.4, 47.9, 45.3, 45.2, 25.1. IR ν/cm⁻¹: 2939(w), 2968(w), 2856(w), 2813(w), 2783(w), 2761(w), 2717(w), 1506(s), 1454(m, 1373(m), 1315(w), 1299(w), 1259(w), 1230(m), 1176(w), 1155(w), 1128(w), 1099(w), 1068(w), 1041(m), 958(m), 819(m). MS: m/z 154.
(100%), 307 (42%), 460 (30%), 631 (M⁺, 68%). Elemental analysis found (calc. for $C_{22}H_{48}S_4N_6Pd$)%: C: 40.84 (41.85), H: 7.47 (7.66), N: 12.56 (13.31). Crystal data: Yellow crystals, size 0.40 × 0.38 × 0.04 mm, monoclinic, space group P2₁/n, a = 17.1576(15) Å, b = 8.5631(7) Å, c = 21.7375(19) Å, β = 110.3170(10)°, V = 2995.0(4) Å³, Z = 4, $d_{\text{calc}}$ = 1.400 g/cm³, $\mu$ = 0.920 mm⁻¹, F(000) = 1328, final R indices [$F^2 > 2\sigma$] $R_1$ = 0.026, $wR_2$ = 0.064, R indices (all data) $R_1$ = 0.030, $wR_2$ = 0.065.

$[\text{Co}S_2CN(CH_2CH_2CH_2NMe_2)_2]_3$ – from cobalt acetate – green solid - yield (0.76 g, 45%). $^1H$ NMR: δ 3.81 (m, 6 H, J ca. 7.2, $S_2CNCH_2$), 3.50 (m, 6 H, J ca. 7.2, $S_2CNCH_2$), 2.28 (t, 12 H, J 6.8, CH$_2$NMe$_2$), 2.19 (s, 36 H, NCH$_3$), 1.84 (t, 12 H, J 6.8, CH$_2$CH$_2$CH$_2$). $^{13}C$ NMR: δ 206.5, 56.6, 46.9, 45.3, 25.3. IR v/cm⁻¹: 2968(w), 2933(w), 2856(w), 2815(w), 2777(w), 2763(w), 2721(w), 1496(s), 1456(w), 1427(w), 1363(m), 1313(w), 1298(w), 1260(w), 1230(m), 1180(w), 1043(m), 989(w), 970(m), 830(w), 760(w), 647(w). MS: m/z 154 (20%), 286 (100%), 393 (48%), 583 (31%), 846 (M⁺, 7%). Elemental analysis found (calc. for $C_{33}H_{72}S_9N_9Co$: C: 47.00 (46.86), H: 8.78 (8.52), N: 14.68 (14.91). Crystal Data: Green block, size 0.28 × 0.26 × 0.21 mm, monoclinic, space group C2/c, a = 22.931(2) Å, b = 10.353(1) Å, c = 19.518(2) Å, β = 101.027(1)°, V = 4547.8(7) Å³, Z = 4, $d_{\text{calc}}$ = 1.236 g/cm³, $\mu$ = 0.686 mm⁻¹, F(000) = 1824, final R indices [$F^2 > 2\sigma$] $R_1$ = 0.029, $wR_2$ = 0.077 R indices (all data) $R_1$ = 0.031, $wR_2$ = 0.079.

Acknowledgements

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References


[29] SADABS; University of Göttingen: Göttingen, Germany, 1997.
Figure 1. Molecular structure of [Ni\{S₂CN(CH₂CH₂NEt₂)₂\}_2] (1)

Figure 2. Molecular structure of [Cu\{S₂CN(CH₂CH₂NEt₂)₂\}_2] (2)
Figure 3. Molecular structure of [Cu\{S₂CN(CH₂CH₂CH₂NMe₂)₂\}₂] (6)

Figure 4. Molecular structure of [Pd\{S₂CN(CH₂CH₂CH₂NMe₂)₂\}₂] (8)
Figure 5. Molecular structure of $[\text{Co}\{S_2\text{CN(CH}_2\text{CH}_3\text{CH}_2\text{NMe}_2\}_2\}_3$] (11)
Graphical abstract

The amine-functionalised dithiocarbamate salts K[\(\text{S}_2\text{CN(CH}_2\text{CH}_2\text{NEt}_2\text{)}_2\)] and K[\(\text{S}_2\text{CN(CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\text{)}_2\)] have been prepared and used for the synthesis of a dithiocarbamate complexes, the molecular structures of \[\text{M}\{\text{S}_2\text{CN(CH}_2\text{CH}_2\text{NEt}_2\text{)}_2\}\] (\(\text{M} = \text{Cu, Ni}\)), \[\text{M}\{\text{S}_2\text{CN(CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\text{)}_2\}\] (\(\text{M} = \text{Cu, Pd}\)) and \[\text{Co}\{\text{S}_2\text{CN(CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2\text{)}_2\}\] being elucidated by X-ray crystallography. No significant intermolecular interactions were found.
Table 1. Selected metric data for [M{S₂CN(CH₂CH₂NEt)₂}₂] (M = Ni, Cu), [M{S₂CN(CH₂CH₂CH₂NMe)₂}₂] (M = Cu, Pd) and [Co{S₂CN(CH₂CH₂CH₂NMe)₂}₃]

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