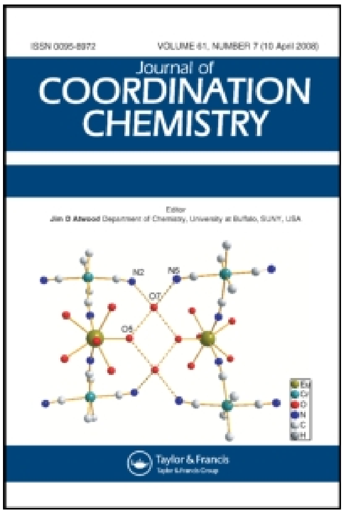

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Synthesis, Crystal Structure and Stability Studies of Dithiocarbamate Complexes of Some Transition Elements (M=Co, Ni, Pd)

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SYNTHESIS, CRYSTAL STRUCTURE AND STABILITY STUDIES OF DITHIOCARBAMATE COMPLEXES OF SOME TRANSITION ELEMENTS (M=Co, Ni, Pd)

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Single-crystal x-ray structure determinations have been recorded at 295 K for the dithiocarbamate metal compounds: $[Co(Et_2dtc)_3]$, $[Co(nPr_2dtc)_3]$, $[Pd(iPr_2dtc)_2]$ and $[Pd(Et_2dtc)_2]$. The stability constants(K) in EtOH of dialkyldithiocarbamate metal complexes $[M(R_2dtc)_n]$ (M = Co, Ni, Pd. R = Me, Et, iPr, nPr. n = 2, 3. dtc = dithiocarbamate) are determined by UV-vis data. The stability of the metal complexes increases in the order: Co < Ni < Pd. The effects of alkyl groups on the stability of $[M(R_2dtc)_2]$ (M = Ni and Pd) increase in the order: Me < Et < nPr < iPr, and $[Co(R_2dtc)_3]$ decrease in the order: Et > iPr > nPr > Me. The results obtained from this study confirm that the stability due to alkyl groups may be partly attributed to changes in the residual positive charge and also partly to steric hindrance of branched alkyl-groups. The comparison between the solid and solution states shows that the $[M(R_2dtc)_2]$ (M = Pd, Ni) complexes have similar changes in M–S distance and stability with change in alkyl group. $[M(iPr_2dtc)_2]$ has the shortest M–S distance and the highest stability in solution.

Keywords: Transition metal; Stability constants; X-ray structure; Dithiocarbamate

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INTRODUCTION

Dialkyl-substituted dithiocarbamate anions have proved to be highly versatile chelating agents for the separation of metals as metal chelates by gas chromatography [1]. Their performance in liquid-liquid extraction and other analytical procedures [2] makes them attractive for the determination of metals by gas chromatography [3]. Some of the dialkyl-substituted dithiocarbamate salts have also shown interesting biological effects which include anti-alkylation [4, 5] or anti-HIV properties [6, 7]. They are also used as effective antidotes for cadmium intoxication [8, 9]. The ability of dtc to bind to metal has been known for many years. It forms a chelate with virtually all transition elements [10]. The bidentate anion is also known to bridge two transition metal centers [11]. Water-soluble dialkyldithiocarbamate complexes have been tested in various medical applications [12].

In recent years, attention has focused on Pd(II) and Ni(II) square-planar complexes owing to the large variety of reactions in which they are involved as catalysts [13]. Further interest has been directed to these complexes since the discovery of the anticancer activity of some of them [14, 15]. Palladium chelates have been used as internal standards in gas chromatographic determinations of metals [16]. We also know that the tris-chelated cobalt (III) complexes of (N,N-disubstituted)dithiocarbamates which are non-charged species and kinetically inert should be resolvable into optical enantiomers [17]. In this paper, we report the stability constants(K) in EtOH of dialkyldithiocarbamate metal complexes $[M(R_2dtc)_n]$ ($M = Co, Ni, Pd$. $R = Me, Et, iPr, nPr$; $n = 2, 3$; dtc = dithiocarbamate) and the crystal structure of $[Pd(iPr_2dtc)_2]$, $[Pd(Et_2dtc)_2]$, $[Co(nPr_2dtc)_3]$ and $[Co(Et_2dtc)_3]$.

EXPERIMENTAL

Synthesis

All chemicals were obtained from a commercial source and used without further purification. Reagents R_2dtcNa ($R = Me, Et, nPr, iPr$) were synthesized by the reaction of R_2NH, NaOH and CS_2 in water.

Preparation of Complexes $[M(R_2dtc)_n]$

To a heated aqueous solution of $Na(R_2dtc)$ [0.01 mol] was added an EtOH solution of metal chloride [$MCl_2 \cdot 6H_2O$, 0.05 mol] with stirring.

The precipitate was collected by filtration, washed with water, and dried over P_4O_{10}. These products were submitted for elemental analysis. Solid $[M(R_2dtc)_n]$ was dissolved in acetone and allowed to evaporate slowly. This resulted in the formation of single crystals which were then used in the crystallographic study. Melting point: $[Pd(Me_2dtc)_2]$, 145°C; $[Ni(Et_2dtc)_2]$, 83 ~ 84°C; $[Pd(Et_2dtc)_2]$, 241 ~ 242°C; $[Ni(nPr_2dtc)_2]$, 122 ~ 123°C; $[Pd(nPr_2dtc)_2]$, 148 ~ 149°C; $[Pd(iPr_2dtc)_2]$, 109°C; The others > 300°C [3, 18].

Equilibrium Studies

UV-vis solution spectra were recorded on a Shimadzu UV-240 spectrophotometer at room temperature. Addition of colorless sodium dialkyldithiocarbamate EtOH solution to the EtOH solution of $[MCl_2]$ promptly forms colored dialkyldithiocarbamate metal complexes, which show an intense characteristic absorption at the wavelength of *ca.* 310 – 320 nm. The stoichiometry and stability constants were determined by the method of Job [19], and calculated by the Benesi-Hildebrand method [20].

X-ray Structure Determination

Information concerning crystallographic data and structure refinement of $[Pd(iPr_2dtc)_2]$, $[Pd(Et_2dtc)_2]$, $[Co(nPr_2dtc)_3]$ and $[Co(Et_2dtc)_3]$ are given in Table I. Reflection data were measured at 20°C using graphite

TABLE I Summary of crystallographic result for some dithiocarbamate metal complexes

Compound	$[Pd(iPr_2dtc)_2]$	$[Pd(Et_2dtc)_2]$	$[Co(nPr_2dtc)_3]$	$[Co(Et_2dtc)_3]$
Formula weight	459.02	402.92	488.72	504.72
Empirical formula	$C_{14}H_{28}N_2PdS_4$	$C_{10}H_{20}N_2PdS_4$	$C_{21}H_{42}CoN_3S_6$	$C_{15}H_{30}CoN_3S_6$
Crystal size (nm)	0.55 × 0.3 × 0.05	0.15 × 0.25 × 0.4	0.36 × 0.36 × 0.3	0.2 × 0.2 × 0.3
Crystal system	Monoclinic	Tetragonal	Rhombohedral	Monoclinic
Space group	P 2 (1)/c	$P4_2/n$	R-3c	C2/c
Unit cell dimensions				
a, Å	8.1731(1)	16.430(2)	10.185(1)	14.113(1)
b, Å	18.1353(1)	16.430(2)	10.185(1)	10.301(1)
c, Å	14.8756(2)	6.239(3)	51.807(4)	17.067(3)
α, deg	90°	90°	90°	90°
β, deg	101.667(1)°	90°	90°	110.17(1)°
γ, deg	90°	90°	120°	90°
Vol. A^3	2159.33(4)	1684.2(7)	4653.9(8)	2329.0(5)
Z	4	4	6	2
D (calcd.) Mg/m^3	1.412	1.589	1.259	1.439
Abs coeff. mm^{-1}	1.242	1.580	0.971	1.280

TABLE I (Continued)

F(000)	944	816	1872	1060
Wavelength Å	0.71073	0.71069	0.71073	0.71073
Temp. K	293(2)	293(2)	293(2)	293(2)
θ range, deg.	2.65 to 24.99	1.95 to 27.45	2.36 to 25.47	2.50 to 30.00
Max. and Min. transmission	0.887 and 0.552	0.8732 and 0.9997	0.747 and 0.618	0.8497 and 0.6728
Rint	0.0239	0.015	0.0353	0.0319
GOF	1.253	1.06	1.027	0.985
Largest diff. peak and hole($e^-/Å^3$)	0.308 -0.473	0.15 -0.51	0.333 -0.313	0.926 -0.845

monochromatic M_o-K_α ($\lambda = 0.71073$ Å) radiation. The collected data were reduced using the program SAINT [21] and empirical absorption corrections were done using the SADABS [22] program. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2_{obs} using the SHELXTL [23] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The molecular graphics were created using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* [24].

RESULTS AND DISCUSSION

Crystal Structure of [Pd(iPr$_2$dtc)$_2$]

The structure of [Pd(iPr$_2$dtc)$_2$] is built up of centro-symmetric monomeric entities. Figure 1 shows a perspective view of the monomeric unit with the atomic numbering scheme. Selected bond distances and angles are listed in Table II.

In the crystal of [Pd(iPr$_2$dtc)$_2$], the asymmetric unit contains a pair of independent half-molecules of the complex [Pd(iPr$_2$dtc)$_2$]. The Pd atoms of these crystallographically independent molecules lie on the inversion center and one half of each molecule is related to the other half by inversion. The two dithiocarbamate ligands coordinate to one Pd atom through the S atoms. The Pd atoms adopt a square-planar geometry and the mean PdS$_4$ planes of the two molecules are almost perpendicular to each other, the dihedral angle being 88.61(2)°. The dimensions within each ligand are normal. The dihedral angles between the PdS$_4$ and S$_2$CNC$_2$ planes are 2.34(4) and 0.07(3)° for A and B, respectively. The bond lengths of S(1A)–Pd(1A) and S(2A)–Pd(1A) are 2.3201(6) and 2.3152(7) Å, respectively; and the bond angles of S(1A)–Pd(1A)–S(2A) and S(1A)–Pd(1A)–S(2AA) are

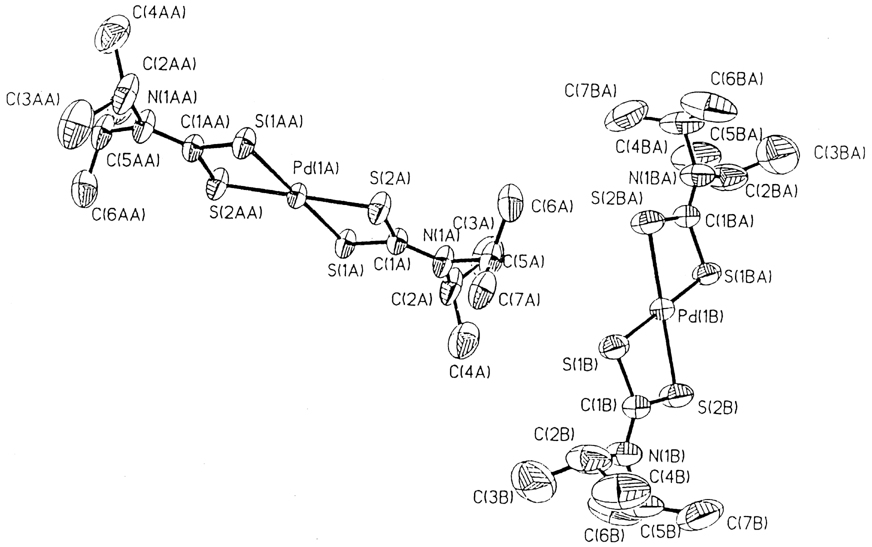

FIGURE 1 Molecular structure for $Pd_2(iPr_2dtc)_4$ with the atomic numbering scheme.

TABLE II Selected bond distances (Å) and bond angles (°) of the title compound

Species	*Atoms*	*Me$_2$dtc*	*Et$_2$dtc*	*iPr$_2$dtc*	*nPr$_2$dtc*
Palladium(II) complexes[a]	Pd–S		2.3180(6)	2.3127(8)	2.323(3)
	S–C		1.718(3)	1.728(3)	1.733(8)
	C–N		1.312(3)	1.313(4)	1.309(8)
	S–C–S		111.5(1)	109.6(2)	111.4(4)
	C–N–C		121.5(2)	116.5(3)	115.4(5)
Nickel(II) complexes[b]	Ni–S	2.200(9)	2.201(6)	2.185(3)	2.202(1)
	S–C	1.72(3)	1.707(6)	1.718(2)	1.720(4)
	C–N	1.349(9)	1.33(1)	1.307(4)	1.309(4)
	S–C–S	109.9(4)	110.3(1)	108.3(2)	109.6(2)
	C–N–C	118.4(5)	116.5(1)	116.3(4)	116.6(9)
Cobalt(III) complexes[c]	Co–S	2.264(3)	2.269(9)	2.26(1)	2.262(3)
	S–C	1.705(1)	1.718(3)	1.71(1)	1.703(5)
	C–N	1.320(4)	1.316(5)	1.32(1)	1.340(9)
	S–C–S	110.4(1)	109.2(2)	108.6(6)	109.9(4)
	C–N–C	117.2(3)	111.5(5)	115(1)	121.6(7)

[a] Data for Et_2 and iPr_2 were taken from this work, and from Riekkola *et al.*, Ref. [3], for nPr_2.
[b] Data from: Healy *et al.*, Ref. [28], for Me_2, Et_2, iPr_2; this work for nPr_2.
[c] Data from: Healy *et al.*, Ref. [28], for Me_2 and iPr_2; this work for Et_2 and nPr_2.

75.09(2) and 104.91(2)°, respectively. All these parameters are in close agreement with those reported before [25–27]. The carbon-sulfur bonds have an average distance of 1.726(3) Å. The ligand "bite" angle S–C–S has a mean value of 109.66(13)°. The N(1A)–C(1A) bond distances [1.316(3) Å] are shorter than other N—C bond distances indicative of considerable double-bond character.

Crystal Structure of [Co(nPr$_2$dtc)$_3$]

The unit cell of [Co(nPr$_2$dtc)$_3$] consists of six discrete monomeric molecules of Co(III) tris(dipropyldithiocarbamate) complexes. X-ray analysis reveals that the Co atom is located on the intersection of the three-fold and two-fold axes which are mutually perpendicular. Each Co is coordinated to three bidentate [S$_2$CNPr$_2$] ligands which are related to one another by a three-fold axis. The central Co atom is octahedrally coordinated by a meridional arrangement of six S atoms. The octahedron is distorted as a result of the forced configuration of the four-membered chelate ring. The average Co–S distance is 2.262(3) Å. The cobalt atom lies on a two-fold axis, which bisects one of the two dithiocarbamate ligands. The atoms in a second dithiocarbamate ligand lie in general positions, but in turn they generate a third dithiocarbamate ligand from the two-fold axis. It is easy to see in Figure 2 that the geometry of the six sulfur atoms surrounding the cobalt are quite distorted from a regular octahedron, as demonstrated by the $S-Co-S^{\#1}$ and $S'-Co-S'^{\#4}$ angles of 165.74(11)° and 166.5(2)°. This distortion from a

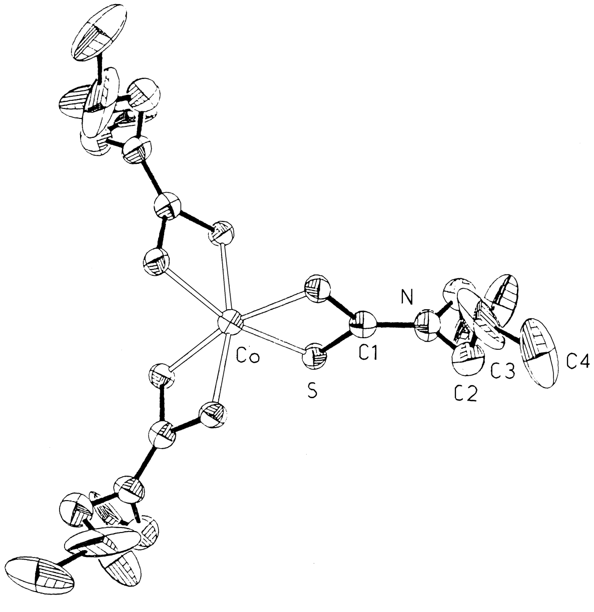

FIGURE 2 Molecular structure for Co(nPr$_2$dtc)$_3$ with the atomic numbering scheme.

perfect octahedron is due primarily to the constraint imposed on the geometry of the molecule by the rigid nature of the dithiocarbamate ligands and by the size of the "bite" angles at the metal, which in this case are $S-Co-S^{\#3} = 76.34(11)^\circ$ and $S'-Co-S'^{\#3} = 76.2(2)^\circ$. A distorted octahedral configuration of the monomeric complex is also seen in other derivatives in this series $[Co(S_2CNR_2)_3]$: $[R = Et, iPr, CH_2Ph]$ [28, 29]. The bond lengths of Co – S in this complex (2.257(3) and 2.266(2) Å) are normal. The N—C(1)bond distance [1.340(9) Å] is shorter than the other N—C bond distance indicative of considerable double-bond character.

The crystal structures of $[Co(Et_2dtc)_3]$ and $[Pd(Et_2dtc)_2]$ are redetermined. Our present results are in general accord with the earlier determination [26, 28], although at a higher level of precision. Selected bond distances and angles are listed in Table II.

Equilibrium Studies in Solution

The equilibrium studies are taken in EtOH solution by adding the ligands to the metal(II) compound. Intensity measurements were taken in the wavelength range 310 – 320 nm. The stoichiometry and stability constants were determined by the method of Job [19], and calculated by the Benesi-Hildebrand method [20]. The equilibrium constants obtained are listed in Table III showing the order of stability of the different alkyl groups in $[Pd(R_2dtc)_2]$ decreases as follows:

$$\mathbf{i - Pr > n - Pr > Et > Me}$$

This order may be partly attributed to changes in the residual positive charge and also partly to the steric hindrance of branched alkyl-groups, but the electronic effects are more important than steric effects in this case. The order of stability of the different alkyl groups in $[Ni(R_2dtc)_2]$ decreased as follows:

$$\mathbf{i - Pr > Et > n - Pr}$$

TABLE III Stability constants of dialkyldithiocarbamate metal complexes in EtOH solution

K_{eq}	$R = Me$	$R = Et$	$R = nPr$	$R = iPr$
$Pd(R_2dtc)_2$	4.07×10^8	1.39×10^9	2.18×10^9	3.06×10^9
$Ni(R_2dtc)_2$	–	6.27×10^7	2.87×10^7	2.42×10^8
$Co(R_2dtc)_3$	3.15×10^{10}	8.08×10^{11}	5.04×10^{10}	6.35×10^{11}

and in [Co(R_2dtc)$_3$] decreased as follows:

$$\mathbf{Et > i - Pr > n - Pr > Me}$$

The important phenomenon is that Co^{2+} is oxidized to Co^{3+} when forming coordinate complexes. This suggests that the unstable coordination complexes [Co(R_2dtc)$_2$] are easily changed to stable coordination complexes [Co(R_2dtc)$_3$], which is the mechanism of irreversible autoxidation reactions of cobalt complexes [30, 29]. This phenomenon is also found in the solid state. [Co(R_2dtc)$_3$] not [Co(R_2dtc)$_2$] is formed when we add a heated aqueous solution of Na(R_2dtc) to an EtOH solution of cobalt(II) chloride.

General Discussion

The [M(R_2dtc)$_2$] (M = Pd, Ni) complexes in solution have similar changes with alkyl groups to the solid state. The M–S distances show small decreases along the series: nPr > Et > Me > iPr, the biggest change being for the diisopropyl complex which has the shortest M–S distance in the solid and the highest stability in solution. The results for the metal(II) complexes are consistent with the increased ligand-field strength of the ligands resulting in shorter M–S distances. The cobalt(III) complexes [Co(R_2dtc)$_3$] are different, [Co(Et_2dtc)$_3$] has the highest stability in solution. It may be that for the cobalt compounds, this effect is overridden by the interligand S...S repulsive forces in the more crowed CoS_6 molecular core. For each series, the C—N and C—S bond lengths show no systematic variation.

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