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INEQUIVALENT COORDINATION OF THIOSEMICARBAZONE LIGANDS IN COBALT (III) AND CHROMIUM (III) COMPLEXES

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Abstract—Chromium (III) and cobalt (III) complexes derived from 2-ketobutyric acid thiosemicarbazone (H_2Kbtsc) have been prepared and characterized. Crystal structure analyses have shown both products to be mixed ligand complexes of the type $M(HKbtsc)(Kbtsc)$ in which the thiosemicarbazone ligand is present in singly deprotonated “thione” and doubly deprotonated “thiol” forms. In each complex, the metal ion is bound to two tridentate ligands in a distorted octahedral geometry with meridional stereochemistry. Small but consistent structural differences between the two types of ligands are observed. Spectroscopic and electrochemical data are consistent with the formulations of these compounds as derived from the crystallographic results.

Transition metal complexes of thiosemicarbazones, $R_1R_2C=N-N(H)-C(S)NH_2$ have been extensively studied and have been the subject of several recent reviews.^{1–3} Thiosemicarbazones have been shown to exhibit a range of types of biological activity which in a number of cases is thought to be related to their ability to chelate trace metals. Also, transition metal complexes of thiosemicarbazones have been found in some instances to have enhanced or modified activity in comparison to the uncomplexed ligands.³ Simple thiosemicarbazones ($R_1 = H$; $R_2 = \text{alkyl or aryl}$) normally bind to transition metals as neutral bidentate ligands, with a five-membered chelate ring formed by metal–sulphur and metal–imine nitrogen bonds. A few cases of monodentate S-binding are known, as are instances of coordination as an anion, formed by deprotonation at the imide nitrogen atom. Tridentate thiosemicarbazone derivatives may be obtained by

incorporating a donor atom into R_1 or R_2 . Here again, the charge on the ligand may vary, depending upon whether the imine nitrogen retains its proton.

The existence of two potential ligands differing only by a single proton on an atom remote from the coordination sites raises the possibility of the presence of two inequivalent ligands—one protonated and one deprotonated—within the same metal complex. Such situations have been known for some time^{4,5} for thiosemicarbazone complexes, but only recently has one been documented by a crystallographic study. A chromium (III) complex of pyruvic acid thiosemicarbazone (pvtsc) was found to contain two inequivalent ligands—a singly charged “thione” and a dinegative “thiol”.⁶ In an attempt to determine whether this is a general phenomenon, a number of complexes of pvtsc and related ligands with trivalent metal ions have been investigated. Here we report complexes of Cr^{3+} and Co^{3+} with inequivalent ligands derived from 2-ketobutyric acid thiosemicarbazone.

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EXPERIMENTAL

Synthesis

Thiosemicarbazide and 2-ketobutyric acid were obtained from Fluka A. G. and used without further purification. 2-Ketobutyric acid thiosemicarbazone (H_2Kbtsc) was prepared as described by Sah and Daniels.⁷ Elemental analyses were performed in the Microanalytical Laboratory of the Department of Chemistry, University of Poona.

$Cr(HKbtsc)(Kbtsc)$. To a slurry of 1.0 g of H_2Kbtsc in 50 cm³ water, 0.5 g of solid $NaHCO_3$ was added with stirring. A solution of 0.76 g of $CrCl_3 \cdot 6H_2O$ in 20 cm³ water was added dropwise. The mixture was stirred for another hour and allowed to stand overnight in a refrigerator. The product precipitated as dark purple needle shaped crystals which were washed with water and acetone. Found: C, 30.2; H, 3.7; S, 15.9; Cr, 13.7. Calc. for $CrC_{10}H_{15}N_6O_4S_2$: C, 30.3; H, 3.8; S, 16.2; Cr, 13.1%.

$Co(HKbtsc)(Kbtsc)$. A procedure similar to that for the chromium complex was followed, with a 1 : 2 metal : ligand ratio. Dark red rod-like crystals were obtained by slow evaporation of the reaction mixture. Found: C, 29.5; H, 4.7; N, 20.6; Co, 14.5. Calc. for $CoC_{10}H_{15}N_6O_4S_2$: C, 30.1; H, 3.7; N, 20.7; Co, 14.5%.

Physical measurements

Infrared spectra were recorded on a Perkin-Elmer 283-B spectrometer as KBr pellets. Visible-UV spectra were recorded on a Shimadzu spectrophotometer. Magnetic susceptibilities were measured at 298 K on a Faraday balance, with $HgCo$

(SCN)₄ used as a calibrant. The molecular susceptibilities were corrected for diamagnetism of the constituent atoms by use of Pascal constants. EPR spectra were determined at 77 K on frozen DMF solutions by use of a JEOL JES-FE3X spectrometer.

Cyclic voltammetry measurements were carried out by use of a Bioanalytical BAS CV-27 system on 10⁻³ M solutions in DMSO with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte. All measurements were made under a dry nitrogen atmosphere with a three electrode configuration and a platinum inlay working electrode and Ag/AgCl reference electrode. The data were collected at 298 ± 1 K.

Crystal structures

All crystallographic data were collected on a Nicolet R3m/V diffractometer. General procedures used in the structure analyses have been described.^{8,9} Crystallographic data are given in Table 1; further details are included with the supplementary material. Solution of the structures was accomplished by a combination of direct and heavy atom methods. Final least-squares refinement included anisotropic thermal parameters for all non-hydrogen atoms. For the chromium complex, hydrogen atoms were included in fixed, idealized positions; for the cobalt complex they were refined with isotropic thermal parameters. The hydrogen atom bound to N(1) was not included until the final cycles of refinement. For each structure, a difference Fourier map prior to the final refinement revealed this atom in a stereochemically reasonable position as its highest positive peak. Computer programs utilized included a local version of the UCLA Cry-

Table 1. Crystallographic data

Formula	$CrC_{10}H_{15}N_6O_4S_2$	$CoC_{10}H_{15}N_6O_4S_2$
Formula wt	399.4	406.3
Space group	$P2_1/c$	$P2_1/n$
<i>a</i>	8.704(1) Å	11.183(1) Å
<i>b</i>	16.160(3) Å	9.050(1) Å
<i>c</i>	11.978(2) Å	16.087(2) Å
β	105.83(1)°	100.21(1)°
<i>V</i>	1620.8(5) Å ³	1602.3(3) Å ³
<i>Z</i>	4	4
<i>D</i> _{calc}	1.637 g cm ⁻³	1.684 g cm ⁻³
<i>T</i> , K	297	294
λ , Mo- <i>K</i> _α	0.71073 Å	0.71073 Å
μ	9.6 cm ⁻¹	13.4 cm ⁻¹
<i>R</i> (<i>F</i> _o)	0.035	0.031
<i>R</i> _w (<i>F</i> _o)	0.053	0.044

Table 2. Bond distances and selected bond angles for Cr(HL) (L)

Distances (Å)				
Cr(1)—S(1)	2.401(1)	Cr(1)—S(11)	2.355(1)	
Cr(1)—O(1)	1.966(3)	Cr(1)—O(11)	1.987(3)	
Cr(1)—N(2)	2.034(3)	Cr(1)—N(12)	2.003(3)	
S(1)—C(1)	1.696(4)	S(11)—C(11)	1.750(4)	
C(1)—N(1)	1.358(5)	C(11)—N(11)	1.321(5)	
C(1)—N(3)	1.321(5)	C(11)—N(13)	1.349(5)	
N(1)—N(2)	1.385(4)	N(11)—N(12)	1.373(4)	
N(2)—C(2)	1.278(5)	N(12)—C(12)	1.302(5)	
C(2)—C(3)	1.529(5)	C(12)—C(13)	1.498(6)	
C(2)—C(4)	1.488(5)	C(12)—C(14)	1.487(6)	
C(3)—O(1)	1.291(5)	C(13)—O(11)	1.292(5)	
C(3)—O(2)	1.220(5)	C(13)—O(12)	1.230(5)	
C(4)—C(5)	1.532(7)	C(14)—C(15)	1.522(7)	
Angles (deg)				
O(1)—Cr(1)—S(1)	160.44(9)	O(11)—Cr(1)—S(11)	161.94(9)	
O(1)—Cr(1)—S(11)	93.24(10)	O(11)—Cr(1)—S(1)	89.33(9)	
O(1)—Cr(1)—N(2)	78.87(12)	O(11)—Cr(1)—N(12)	79.87(12)	
O(1)—Cr(1)—N(12)	96.31(12)	O(11)—Cr(1)—N(2)	95.90(13)	
N(2)—Cr(1)—S(1)	81.83(9)	N(12)—Cr(1)—S(11)	82.08(10)	
N(2)—Cr(1)—S(11)	102.15(10)	N(12)—Cr(1)—S(1)	102.70(10)	
S(1)—Cr(1)—S(11)	93.89(4)	O(1)—Cr(1)—O(11)	89.50(12)	
N(2)—Cr(1)—N(12)	173.68(13)			
Cr(1)—S(1)—C(1)	96.7(1)	Cr(1)—S(11)—C(11)	94.5(1)	
Cr(1)—O(1)—C(3)	117.1(2)	Cr(1)—O(11)—C(13)	115.5(2)	
C(1)—N(1)—N(2)	116.6(3)	C(11)—N(11)—N(12)	111.7(3)	
C(2)—N(2)—N(1)	121.5(3)	C(12)—N(12)—N(11)	118.6(3)	
Cr(1)—N(2)—C(2)	117.3(2)	Cr(1)—N(12)—C(12)	115.9(3)	
Cr(1)—N(2)—N(1)	121.2(2)	Cr(1)—N(12)—N(11)	125.1(2)	
S(1)—C(1)—N(1)	123.1(4)	S(11)—C(11)—N(11)	126.6(3)	
N(2)—C(2)—C(3)	111.4(3)	N(12)—C(12)—C(13)	112.8(3)	
C(2)—C(3)—O(1)	114.7(3)	C(12)—C(13)—O(11)	115.5(4)	
Potential hydrogen bonding contacts A—H...B				
		H—B	A—B	A—H—B
N(1)—H(1A)...O(11)	(-x, -y, -z)	1.85	2.72	142
N(3)—H(3B)...O(2)	(x-1, y, z)	1.98	2.88	179
N(13)—H(13A)...O(12)	(1-x, -y, -z)	2.18	2.92	140

stallographic Computing Package,¹⁰ MITHRIL¹¹ and the molecular graphics portions of the SHELXTL package.¹²

Final atomic parameters for nonhydrogen atoms have been deposited and selected bond distances and angles are tabulated in Tables 2 and 3. Full tables of all other crystallographic results are included with the supplementary material.

RESULTS AND DISCUSSION

Crystal structures

The overall molecular structures of the chromium and cobalt complexes, illustrated in Figs. 1 and 2,

are the same. The metal ion is bound to two tridentate ligands in a distorted octahedral geometry with meridional stereochemistry. The pair of five-membered chelate rings that results for each ligand is approximately planar (maximum deviations ranging from 0.036 to 0.090 Å) and the two chelate planes are essentially perpendicular [dihedral angles = 90.6° (M=Cr) and 87.1° (M=Co)] in each complex. The angular distortions from regular octahedral geometry are somewhat greater for the chromium complex, as are the metal–ligand distances.

Evidence for protonation at N(1) and not at N(11) includes charge balance requirements, location of the protons on final difference Fourier maps (and refinement of the hydrogen coordinates

Table 3. Bond distances and selected bond angles for Co(HL)(L)

Distances (Å)			
Co(1)—S(1)	2.208(8)	Co(1)—S(11)	2.197(7)
Co(1)—O(1)	1.957(2)	Co(1)—O(11)	1.925(2)
Co(1)—N(2)	1.889(2)	Co(1)—N(12)	1.884(2)
S(1)—C(1)	1.705(2)	S(11)—C(11)	1.752(2)
C(1)—N(1)	1.347(3)	C(11)—N(11)	1.323(3)
C(1)—N(3)	1.306(4)	C(11)—N(13)	1.334(3)
N(1)—N(2)	1.367(3)	N(11)—N(12)	1.364(2)
N(2)—C(2)	1.271(3)	N(12)—C(12)	1.294(3)
C(2)—C(3)	1.514(4)	C(12)—C(13)	1.505(3)
C(2)—C(4)	1.496(3)	C(12)—C(14)	1.492(3)
C(3)—O(1)	1.279(3)	C(13)—O(11)	1.263(3)
C(3)—O(2)	1.226(3)	C(13)—O(12)	1.238(3)
C(4)—C(5)	1.514(5)	C(14)—C(15)	1.510(5)
Angles (deg)			
O(1)—Co(1)—S(1)	170.20(5)	O(11)—Co(1)—S(11)	170.15(5)
O(1)—Co(1)—S(11)	91.60(6)	O(11)—Co(1)—S(1)	91.24(6)
O(1)—Co(1)—N(2)	82.57(8)	O(11)—Co(1)—N(12)	83.90(7)
O(1)—Co(1)—N(12)	97.43(8)	O(11)—Co(1)—N(2)	90.31(7)
N(2)—Co(1)—S(1)	87.72(6)	N(12)—Co(1)—S(11)	86.49(6)
N(2)—Co(1)—S(11)	99.31(6)	N(12)—Co(1)—S(1)	92.11(6)
S(1)—Co(1)—S(11)	91.24(3)	O(1)—Co(1)—O(11)	87.55(8)
N(2)—Co(1)—N(12)	174.20(8)	Co(1)—S(11)—C(11)	94.6(2)
Co(1)—S(1)—C(1)	95.8(2)	Co(1)—O(11)—C(13)	112.7(1)
Co(1)—O(1)—C(3)	112.1(2)	C(11)—N(11)—N(12)	111.3(2)
C(1)—N(1)—N(2)	117.3(2)	C(12)—N(12)—N(11)	120.9(2)
C(2)—N(2)—N(1)	123.6(2)	Co(1)—N(12)—C(12)	115.3(2)
Co(1)—N(2)—C(2)	117.3(2)	Co(1)—N(12)—N(11)	123.6(1)
Co(1)—N(2)—N(1)	118.6(2)	S(11)—C(11)—N(11)	124.1(2)
S(1)—C(1)—N(1)	120.4(2)	N(12)—C(12)—C(13)	112.0(2)
N(2)—C(2)—C(3)	111.6(2)	O(11)—C(13)—O(12)	122.8(2)
O(1)—C(3)—O(2)	125.1(3)	C(12)—C(13)—O(12)	121.1(2)
C(2)—C(3)—O(2)	119.2(2)	C(12)—C(13)—O(11)	116.1(2)
C(2)—C(3)—O(1)	115.8(2)		
Potential hydrogen bonding contacts A—H...B			
		H—B	A—B
N(1)—H(1A)...O(12)	(1/2-x,y-1/2,1/2-z)	2.12	2.90
N(3)—H(3A)...O(2)	(x-1/2,1/2-y,z-1/2)	1.98	2.79
N(13)—H(13A)...O(12)	(x,y-1,z)	2.05	2.92

for the cobalt complex), stereochemical differences between the protonated and deprotonated ligands, and hydrogen bonding considerations. In both complexes, the protonated ligand has a longer N(1 or 11)—C distance, a longer C—NH₂ distance, a shorter C—S distance, and larger C—N—N angles. Exactly the same trends were observed in a previously reported thione/thiol complex of chromium (III). Additional minor differences in bond distances and angles between the two types of ligand are not consistent for the three analogous compounds and must therefore be attributed to other factors. Specifically, there is no clear-cut trend in the

metal—ligand distances, although taken as a whole, these distances are slightly shorter for the thiol than for the thione ligand.

Comparison of ligand bond distances and angles with those in uncomplexed H₂Kbtsc¹³ reveals only small differences; as expected, these are in general greater for the thiol than for the thione ligand. Among the larger changes are a compression of the C(11)—N(11)—N(12) angle and an opening for the S(11)—C(11)—N(11) angle. The chelating ligand adopts the Z-configuration about the C(2)—N(2) and C(1)—N(1) bonds in contrast to the E-configuration found in the free ligand.

Fig. 1. Molecular structure of Cr(HKbtsc)(Kbtsc). Thermal ellipsoids of nonhydrogen atoms are drawn at the 50% probability level.

The details of the molecular packing of the cobalt and chromium complexes are different, but hydrogen bonds play a role in both cases. Likely hydrogen bonding contacts are included in Tables 2 and 3. In each compound, the proton bound to N(1) participates in a hydrogen bond but there are no contacts appropriate for hydrogen bonding involving N(11). This and other asymmetries in hydrogen bonding provide a possible explanation for the lack of disorder involving the closely similar thione and thiol ligands.

Electronic spectra

The UV-vis spectra of the two metal complexes show the expected number of peaks—two and three, respectively for $M = \text{Co}^{3+}$ and $M = \text{Cr}^{3+}$.

Fig. 2. Molecular structure of Co(HKbtsc)(Kbtsc). Thermal ellipsoids of nonhydrogen atoms are drawn at the 50% probability level.

Assignment of these peaks and analysis of their frequencies in the usual manner¹⁴ yields 10 Dq values similar to those previously obtained for similar complexes.^{3,15-18} The results are summarized in Table 4.

Infrared spectra

A number of the characteristic frequencies observed in the parent thiosemicarbazone H_2Kbtsc are shifted to lower values in the Cr and Co complexes. These include the C=O stretching frequency (1690 cm^{-1} in H_2Kbtsc , 1660 cm^{-1} for $M = \text{Cr}^{3+}$, 1640 cm^{-1} for $M = \text{Co}^{3+}$), the C=N bond (1610 cm^{-1} in the free ligand, 1570 cm^{-1} for $M = \text{Cr}$, 1585 cm^{-1} for $M = \text{Co}$), and the C=S stretch (870 cm^{-1} in the free ligand, 820 cm^{-1} for $M = \text{Cr}^{3+}$ and 810 cm^{-1} for $M = \text{Co}^{3+}$). A medium intensity band at $860\text{--}870\text{ cm}^{-1}$, not present in free H_2Kbtsc , can be attributed to the coordinated thiol. This band was also observed for an iron complex with inequivalent thiosemicarbazone ligands.¹⁹

Magnetic and EPR data

The magnetic moment of the chromium complex is 4.34 B.M., consistent with expectations for a d^3 system. The isotropic EPR signal in frozen DMF solution (Fig. 3) is also typical for trivalent chromium in an octahedral environment.²⁰ The spin-orbit coupling constant λ , as determined from the g and Δ values by the usual relationship²¹ is 28 cm^{-1} . The reduction of λ to 30% of its free-ion value of 92 cm^{-1} reflects the π -acceptor character

Fig. 3. X-band EPR spectrum of Cr(HKbtsc)(Kbtsc) in frozen DMF solvent.

of the thiosemicarbazone ligands. As expected, the cobalt complex is diamagnetic.

Electrochemistry

As shown in Fig. 4, the chromium complex exhibits three successive reduction peaks (-1.02 V, -1.12 V, -1.59 V vs Ag/AgCl), none of which show counterparts on the reverse anodic scans. Comparisons of these values with those of -0.72 V and -1.25 V for the parent ligand suggests that the first two correspond to ligand-based reductions, while the most negative peak arises from an irreversible metal-based reduction. The cobalt (III) complex exhibits a reversible one-electron reduction peak at -0.910 V. This is interpreted as a metal-based reduction; its potential may be compared with that of -0.55 V for an iron (III) complex with similar ligands.²² An irreversible reduction at -1.20 V probably corresponds to the reduction of the coordinated azomethine linkage of the thiosemicarbazide group. This is a slightly more positive potential than that of -1.25 V assigned to reduction of this function in the free ligand. Comparable reductions are observed for many thiosemicarbazones.²³ In a series of thiosemicarbazone complexes of copper (II), a lower value of this potential has been suggested to be correlated with higher biological activity.²⁴

Fig. 4. Cyclic voltammograms (25°C, scan rate 100 mV/s) at a Pt electrode of 10^{-3} M solution in DMSO containing 0.1 M tetraethylammonium perchlorate. All voltages measured with respect to a Ag/AgCl electrode. (a) H_2Kbtsc ; (b) Cr(HKbtsc)(Kbtsc); (c) Co(HKbtsc)(Kbtsc).

Summary

This work shows that the coordination of chemically inequivalent thione/thiol ligands observed earlier in a pyruvic acid thiosemicarbazone complex of chromium (III) appears to be a general phenomenon for complexes of such ligands with trivalent transition metal ions. Such complexation is promoted under neutral conditions and is not influenced by the initial source of the metal ions. The substituent on the C(2) carbon atom influences the bite distance of the ligand and the extent of deformation from octahedral geometry. Electrochemical profiles of both complexes show ligand and metal-based redox peaks.

Supplementary material available

Full tables of experimental details of the crystallographic studies, atomic parameters, aniso-

Table 4. Visible/ultraviolet spectra^a

	M = Cr ³⁺	M = Co ³⁺
Frequency	18796 ($^4A_{2g} \rightarrow ^4T_{2g}$)	14647 ($^1A_{1g} \rightarrow ^1T_{1g}$)
assignment	26315 ($^4A_{2g} \rightarrow ^4T_{1g}(F)$)	21186 ($^1A_{1g} \rightarrow ^1T_{2g}$)
	28985 ($^4A_{2g} \rightarrow ^4T_{1g}(P)$)	
10 Dq	18,800	16,277
B	692	409

^aAll frequencies in cm^{-1} .

tropic displacement parameters, and bond distances and angles are available upon request from RJD.

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