Electrochemical, spectroscopic and structural characterization of the *mer* isomer of ammonium bis(pyruvic acid thiosemicarbazone)cobalt(III)·benzene

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Abstract

The crystal structure is reported of ammonium bis(pyruvic acid thiosemicarbazone)cobalt(III)·benzene, Co-$S_2O_4N_6C_{16}H_{16}$, which forms dark red triclinic crystals with unit cell parameters: $a = 9.307(2)$, $b = 9.555(2)$, $c = 14.729(3)$ Å, $\alpha = 67.04(1)$, $\beta = 118.89(2)$, $\gamma = 79.09(1)°$, $V = 932.9(2)$ Å^3, space group $P\bar{1}$. The final R factor for 3948 observed reflections is 3.1%. The distorted octahedral complex is held together by a hydrogen bonding system involving the ammonium and amine protons and the carboxylate oxygen and imine nitrogen atoms. The coordination polyhedron around the cobalt atom in the complex anion $[Co(PVATSCH)_2]^-$ is highly distorted from regular octahedral geometry as evidenced by the fact that the bond angles about the cobalt atom range from 83.40(6) to 96.75(5)°. The isolated *meridional* isomer contains a *cis* placement of the sulfur donor atoms with puckered ligand moieties arising from the non-planar hydrazinic chain with a folding angle of *ca.* 4° across the sulfur–nitrogen and oxygen–nitrogen atoms. The ligand H₂PVATSC provides a strong ligand field and thus results in a low spin cobalt(III) complex. The complex undergoes a reversible one-electron reduction at the metal center.

Introduction

Transition metal complexes of thiosemicarbazones exhibit a wide variation in their bonding modes and stereochemistries [1–4] where the beneficial antitumor [5], antiviral [6], antimalarial [7], and other medicinal activities [8] have been shown to be related to their metal complexing ability [9].

Recent investigations have shown that thiosemicarbazones having a third potential donor atom (e.g. phenolic or carboxylic hydroxyl, pyridyl nitrogen, etc.) have the most significant medicinal activity [10]. As part of a program concerned with the relationship between the structure and pharmacological activity of tridentate and dibasic thiosemicarbazone complexes, we describe here the structure of a cobalt(III) complex of pyruvic acid thiosemicarbazone (H2PVATSC, **I**), [NH₄][Co(PVATSCH)₂]·C₆H₆ (**II**) which confirms a distorted octahedral geometry for its *mer* isomer and coordination via the thiol mode.

Experimental

Materials

CoCl₂·6H₂O and thiosemicarbazone were obtained from E. Merck. Pyruvic acid was purchased from Fluka Chemical Company. The thiosemicarbazone derivative of pyruvic acid was synthesized by a known procedure [11].

Preparation of mer-NH₄[Co(PVATSCH)₂]·C₆H₆

The complex was prepared by the interaction of CoCl₂·6H₂O and H₂PVATSC in an aqueous medium employing a metal:ligand ratio of 1:2 according to the procedure described by Ablov *et al.* [12]. Dark red rod-like crystals of the title complex suitable for X-ray crystallography were obtained by slow diffusion in a pyridine–benzene solvent system. *Anal.* Calc. for CoS₂O₄N₆C₁₆H₁₆: C, 35.51; H, 4.25; N, 16.57; S, 13.5; Co, 12.45. Found: C, 34.92; H, 4.21; N, 16.57; S, 13.04; Co, 13.01%.

Instrumentation

Electronic absorption spectra were obtained with an Hitachi 220A spectrophotometer using 10 mm rectan-

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gular quartz cell. IR spectra were recorded in nujol mulls on a Perkin-Elmer 283-B IR spectrophotometer using KBr cells. Cyclic voltammetric experiments were performed on a BAS CV-27 assembly in conjunction with an X-Y recorder. Measurements were made on the degassed 10 mM solutions (N_2 bubbled for 15 min prior to measurements) in DMSO containing 0.01 mM tetraethyl ammonium perchlorate as a supporting electrolyte. The working electrode system consisted of a platinum inlay electrode referenced with an Ag/AgCl electrode and a platinum wire as auxiliary electrode.

X-ray data collection

The crystal was mounted in a random orientation to the end of a glass fiber using 5 min epoxy cement and transferred to a goniometer head. Preliminary crystal parameters* and reflection data were obtained and processed by standard methods (see Table 1) [13, 14] on a Nicolet P3m microprocessor controlled four circle X-ray diffractometer and Molecular Structure Corporation's Texray 234 stand-alone crystallographic computing system [15].

Data was collected using the θ–2θ mode with scans of 0.85° above and below Kα and Kα_2 using molybdenum radiation with a graphite monochromator. All non-equivalent reflections in the range $2 < \theta < 30°$ were collected. The intensities of four standard reflections monitored every 96 reflections showed no greater fluctuations than would be expected from Poisson statistics. The structure was solved by direct methods which located the cobalt and sulfur atoms and the rest of the remaining atoms (including hydrogen atoms) were located by successive full-matrix least-squares refinement followed by difference Fourier analyses (the hydrogen atoms on the ammonia nitrogen could not be located by this method and so were not included). All non-hydrogen atoms were refined anisotropically while the hydrogen atoms were refined isotropically.

Results and discussion

Structural results

The molecular structure of the cobalt(III) complex is constructed from the discrete ammonium cations and the 'winged' complex [Co(PVATSCH)$_2$] anions. The positional parameters for all atoms are listed in Table 2 while Fig. 1 shows the distorted octahedral geometry of the cobalt in the anion. It can be seen that each ligand coordinates in a tridentate manner to the central cobalt atom in a doubly deprotonated thiol form yielding a *meridional* isomer. The preference for this geometry

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*Niggli reduced cell is: 9.555(2), 10.906(2), 9.307(3) Å; 92.01(1), 100.91(2), 100.82(1)°.

probably results from the conjugation in the thiosemicarbazone side chain leading to a planar tridentate ligand which in turn imposes a small bite size during chelate formation [16]. The structure is held together by an extensive system of hydrogen bonds involving protons from the ammonium ion and the free amine groups of the ligand as donors and the carboxylate oxygen and imine nitrogen atoms as acceptors.

As a result, the orientation of the sulfur and oxygen donor atoms in the resulting complex is *cis* while that of the nitrogen atoms is *trans*. It is evident from the bond distances and bond angles (Table 3 and 4) that the environment about the cobalt atom is considerably distorted from ideal octahedral geometry. For example, the S–Co–O1 and S–Co–O1' angles are 169.62(4) and 169.50(4)°, respectively, as a result of the small bite size of the ligand, while all other angles appear to be less affected.

Although coordinating PVATSC ligands are mutually perpendicular to each other, the sulfur and oxygen donor atoms that occupy *cis* positions around the cobalt atom constitute the base of a tetrahedron rather than a rectangle with an angle of 14.54(8)° between the O1–Co–O1' and S–Co–S' planes. This is in comparison to values observed in other tridentate bis-thiosemicarbazone complexes (see Table 5) where values ranging from 1.24 [17] to 30.83° [18] can be found. It seems that this tetrahedral deformation is influenced by the displacement of the sulfur and oxygen atoms from the principle equatorial plane containing the Co, S, S', O1 and O1' atoms by 0.170(1) and 0.198(1) Å, respectively.

There are relatively few crystal structures of metal thiosemicarbazone complexes with which to compare these observations [16–24]. The best comparison can be made with the six-coordinate ferric of dichloro-salicylaldehyde thiosemicarbazone [22] which also shows a maximum displacement of c., 0.18 Å for the sulfur and oxygen atoms. Two other planes, viz. those containing the Co, S, O1, N2, N2' and Co, S', O1', N2, N2' atoms exhibit a much smaller deviation (0.044(4) Å).

The coordination polyhedra constructed around the central cobalt atom consists of two five-membered chelate rings (A and B) which are tilted towards each other by an angle of 4.7(2) and 2.3(1)° in the two ligands. The non-planarity of the hydrazinic chain and the small bend across the lines S–N2 and N2–O1 in the two chelate rings lead to such a puckering of the coordinated ligands [25].

When coordinating in the thiol form, the negative charge (generated upon deprotonation) on the thiolato chromophore is delocalized in the N2–N1–C1 system as indicated by their intermediate bond distances (see Table 3) with the primary effect seen in the C–N bonds. The adjacent N–N bond distances, on the other hand,

TABLE 1. Crystal data for $(NH_4)[Co(PVATSCH)_2] \cdot C_6H_6$

Cell constant	
a (Å)	9.307(2)
b (Å)	9.555(2)
c (Å)	14.729(3)
α (°)	67.04(1)
β (°)	118.89(2)
γ (°)	79.09(1)
V (Å^3)	932.9(2)
No. measured reflections	5193
No. $> 3\sigma(F)$	3948
Standards	4 standard reflections measured every 96 reflections
R_{int}	0.025
Range of h	-10 to 11
Range of k	-12 to 13
Range of l	0 to 20
$\sin (\theta/\lambda)_{max}$	0.7049
Formula weight	472.39
$F(000)$	478
Z	2
D_{calc} (g/cm^3)	1.682
Absorption coefficient (cm^{-1})	11.709
Radiation used	Mo Kα
Space group	$P\bar{1}$
p Factor	0.03
Weighting scheme	$w = 4(F_o)^2/\sigma(F_o)^2$, where $\sigma(F_o)^2 = [(\sigma(I))^2 + (p \times (F_o)^2)^2]$
No. atoms refined	46
No. variables	327
Refinement method	based on F
R Factor	0.031
Weighted R factor	0.037
Error (obs) of unit weight	1.47
Maximum shift/error	0.14
Empirical absorption correction applied	
Absorption coefficient: max., min., av.	0.7802, 1.1219, 0.9888
Diffractometer used	Nicolet P3m controlled by Data General Nova 4/c
Data processing system	Molecular Structure Corporation Texray-234 based on a PDP 11/73
Solution method	direct methods (MULTAN 82)
2θ Limits (°)	4.0–60.0
Highest peak in difference Fourier (e/cm^3)	0.4
Lowest peak in difference Fourier (e/cm^3)	0.3

are not much affected. That the thiol form of the ligand is present for both coordinated ligands can be confirmed from the close similarity in bond lengths and angles in the two ligands, from charge considerations, and from the values of the C1–S and C1'–S' bond distances (1.734(2) Å for both). The maximum lengthening of this linkage, 1.775(17) Å, has been observed [24] in the complex Cs[Fe(tsa)$_2$], where tsa is the dianion of salicylaldehyde thiosemicarbazone.

Further confirmation of thiol coordination comes from the cobalt–sulfur distance, 2.203(1) Å, which is less than the sum of their covalent radii and is also the shortest bond length observed for bis-chelates of thiosemicarbazones (see Table 6). For compounds containing thiolato sulfur atoms, Co–S bond lengths range in value from 2.22 [26] to 2.28 [27] (Å) while for complexes containing the thione form these distances typically range from 2.28 [28] to 2.31 [29] Å. The metal

nitrogen distances in the present complex are also short, 1.887(1) and 1.883(1) Å, compared to the average values found in metal thiosemicarbazone complexes (see Table 6) but are similar to those found in the cobalt(III) complex [Co(DTO)(DTOH)] (DTOH = diacetylmonooxime thiosemicarbazone) where values of 1.888(3) and 1.874(3) Å are found [30]. The much shorter values for the metal donor atom distances found in the present complex are reflective of both the rigidity of the coordinating PVATSC moiety as well as the tetrahedral distortions arising from the small bite size of the ligand.

Spectroscopic results

The IR spectrum of the H$_2$PYATSC ligand exhibits asymmetric and symmetric carboxylate modes in the region 1690–1720 cm^{-1} which are displaced by about 80 cm^{-1} to lower wavenumbers indicating the participation of the carboxylate function in coordination to

TABLE 2. Positional parameters and their e.s.d.s for (NH_4)-$[Co(PVATSCH)_2]\cdot C_6H_6$

Atom	x	y	z	B (Å^2)
Co	0.56381(4)	0.09401(3)	0.19170(2)	1.548(6)
S	0.57802(8)	−0.10267(7)	0.14889(4)	2.14(1)
S'	0.75680(7)	0.14701(7)	0.15498(5)	2.15(1)
O1'	0.3562(2)	0.0869(2)	0.1947(1)	2.41(4)
O1	0.5779(2)	0.2340(2)	0.2615(1)	2.27(4)
O2'	0.0461(2)	0.2239(3)	0.0650(2)	4.26(6)
O2	0.7219(3)	0.1972(2)	0.4479(2)	4.07(6)
N1	0.8232(2)	−0.2604(2)	0.4013(1)	1.95(5)
N1'	0.4027(2)	0.3766(2)	−0.0560(1)	1.74(4)
N2'	0.3728(2)	0.2831(2)	0.0255(1)	1.61(4)
N2	0.7462(2)	−0.0898(2)	0.3614(1)	1.68(4)
N3	0.8005(3)	−0.4319(2)	0.3266(2)	2.74(6)
N3'	0.6355(2)	0.3989(2)	−0.0663(2)	2.18(5)
N(H4)	0.4562(3)	0.9122(4)	0.4353(2)	4.83(8)
C1'	0.5839(3)	0.3198(2)	0.0004(2)	1.72(5)
C1	0.7458(3)	−0.2740(3)	0.3040(2)	1.88(5)
CB1	0.2950(4)	0.7284(4)	0.2401(3)	4.76(9)
C2	0.7891(3)	−0.0494(3)	0.4418(2)	1.93(5)
CB2	0.3890(4)	0.5526(4)	0.3172(2)	4.41(8)
C2'	0.2061(3)	0.3258(3)	−0.0101(2)	1.98(5)
C3	0.6909(3)	0.1409(3)	0.3822(2)	2.23(6)
C3'	0.1974(3)	0.2063(3)	0.0880(2)	2.41(6)
CB3	0.3573(4)	0.4702(3)	0.3975(2)	3.55(8)
C4'	0.0372(3)	0.4769(4)	−0.1341(2)	3.13(7)
C4	0.9152(4)	−0.1735(3)	0.5799(2)	3.07(7)
CB4	0.2358(4)	0.5596(5)	0.4031(3)	5.2(1)
CB5	0.1431(4)	0.7336(5)	0.3283(3)	5.2(1)
CB6	0.1718(4)	0.8200(4)	0.2456(3)	4.07(9)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)$-$[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.
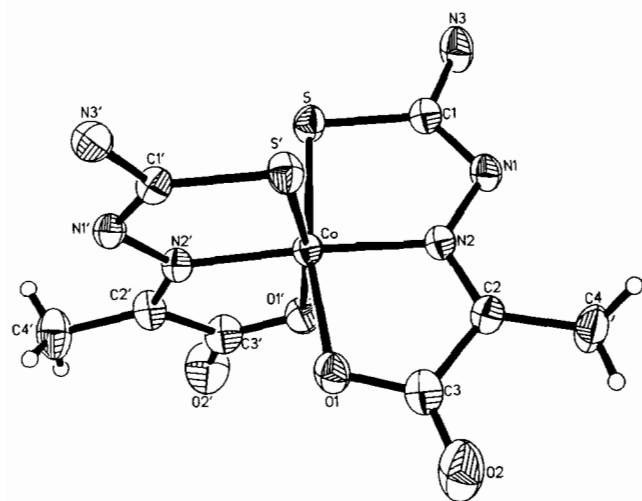

Fig. 1. Structural diagram for the bis(pyruvic acid thiosemicarbazone)cobalt(III) anion.

the metal [31]. Involvement of the azomethine nitrogen in complexation can be seen from the lowering of $\nu(C=N)$ from 1610 cm^{-1} in the free ligand to 1580

TABLE 3. Interatomic distances (Å) for $(NH_4)[Co(PVA$-$TSCH)_2]\cdot C_6H_6$ with e.s.d.s in parentheses

Co–S	2.204(1)	Co–S'	2.201(1)
Co–O1'	1.967(1)	Co–O1	1.968(1)
Co–N2'	1.883(1)	Co–N2	1.887(1)
S–C1	1.734(2)	S'–C1'	1.738(2)
O1'–C3'	1.294(2)	O1–C3	1.289(2)
O2'–C3'	1.238(3)	O2–C3	1.227(2)
N1–N2	1.385(2)	N1–C1	1.331(2)
N1'–N2'	1.376(2)	N1'–C1'	1.332(2)
N2'–C2'	1.288(2)	N2–C2	1.292(2)
N3–C1	1.341(2)	N3'–C1'	1.334(2)
C2–C3	1.505(3)	C2'–C3'	1.502(3)
C2–C4	1.485(3)	C2'–C4'	1.483(3)
C1B–C2B	1.368(4)	C2B–C3B	1.342(4)
C3B–C4B	1.340(4)	C4B–C5B	1.353(5)
C5B–C6B	1.361(4)	C6B–C1B	1.362(4)

TABLE 4. Bond angles (°) for $(NH_4)[Co(PVATSCH)_2]\cdot C_6H_6$ with e.s.d.s in parentheses

S–Co–S'	91.72(2)	S–Co–O1'	90.99(5)
S–Co–O1	169.62(4)	S–Co–N2'	96.15(5)
S–Co–N2	86.42(5)	S'–Co–O1'	169.50(4)
S'–Co–O1	91.49(5)	S'–Co–N2'	86.04(5)
S'–Co–N2	96.75(5)	O1'–Co–O1	87.62(6)
O1'–Co–N2'	83.58(6)	O1'–Co–N2	93.54(6)
O1–Co–N2'	93.92(6)	O1–Co–N2	83.40(6)
N2'–Co–N2	176.16(7)	Co–S–C1	94.57(7)
Co–S'–C1'	95.11(7)	Co–O1'–C3'	111.6(1)
Co–O1–C3	112.1(1)	Co–N2'–N1'	124.1(1)
Co–N2–N1	123.6(1)	Co–N2'–C2'	116.1(1)
Co–N2–C2	115.8(1)	N2–N1–C1	110.4(1)
N2'–N1'–C1'	110.9(1)	N1'–N2'–C2'	119.8(2)
N1–N2–C2	120.4(2)	S'–C1'–N1'	123.8(1)
S–C1–N1	125.0(1)	S'–C1'–N3'	118.1(2)
S–C1–N3	116.9(2)	N1'–C1'–N3'	118.1(2)
N1–C1–N3	118.1(2)	N2–C2–C3	113.3(2)
N2'–C2'–C3'	113.0(2)	N2–C2–C4	125.4(2)
N2'–C2'–C4'	124.7(2)	C3–C2–C4	121.3(2)
C3'–C2'–C4'	122.2(2)	O1–C3–O2	124.8(2)
O1'–C3'–O2'	123.8(2)	O1–C3–C2	115.2(2)
O1'–C3'–C2'	115.6(2)	O2–C3–C2	120.0(2)
O2'–C3'–C2'	120.7(2)	C2B–C1B–C6B	120.3(3)
C1B–C2B–C3B	119.7(3)	C2B–C3B–C4B	120.2(3)
C3B–C4B–C5B	120.8(3)	C4B–C5B–C6B	120.1(3)
C5B–C6B–C1B	118.8(3)		

cm^{-1} in the complex. The prominent absorption at 860 cm^{-1} characteristic of the thione form of the ligand in the solid state is absent from the spectrum of the complex indicating that the ligand is coordinating in its thiol form.

For the present diamagnetic cobalt(III) complex measured in DMF solution, two of the possible three electronic transitions for octahedral cobalt are observed at 15 673 (ν_1) and 20 408 (ν_2) cm^{-1} assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively. The crystal field parameters calculated for this compound using established spectral fingerprint relations [32] are

TABLE 5. Comparison of selected bond angles (°) in the coordination sphere of bis-thiosemicarbazone metal complexes

Angle	Co[a]	Ni [19]	Cr [20]	Cr [16]	Cr [21]	Fe [22]	Fe [23]	Fe [17]	Fe [24]	Co [30]	Ni [18]	Average value
S-M-S'	91.72(2)	96.2(1)	93.1(1)	94.25(4)	93.5	89.4(1)	91.4(2)	93.8(1)	100.3(2)	91.59(6)	96.1(1)	93.76(2.97)
S-M-N	86.42(5)	81.1(2)	82.0(1)	81.66(8)	77.9	83.4(3)	81.1(3)	85.8(2)	78.4(4)	86.2(2)	80.7(2)	82.24(4.18)
S-M-N'	96.15(5)	100.6(2)	90.4(1)	105.97(8)	107.6	93.6(3)	95.4(5)	91.4(2)	87.2(4)	92.3(2)	102.8(2)	96.67(6.68)
S-M-O	169.62(4)	158.9(2) (N)	171.2(1)	162.37(8)	161.6	175.1(2)	169.8(4)	176.2(2)	161.3(4)	167.8(2) (N)	158.1(2) (N)	166.57(6.39)
S-M-O'	90.99(5)	89.5(2)	91.1(1)	90.58(7)	89.2	91.5(2)	88.2(3)	89.9(2)	89.4(4)	91.3(2) (N)	93.2(2) (N)	90.44(1.38)
S'-M-N	96.75(5)	100.4(2)	95.7(1)	97.39(8)	108.2	92.7(3)	93.5(4)	91.4(2)	89.9(4)	94.9(2)	110.9(2)	97.43(6.69)
S'-M-N'	86.04(5)	81.3(2)	81.5(1)	81.92(8)	79.9	85.1(3)	81.3(4)	85.8(2)	78.9(4)	85.9(2)	79.3(3)	83.36(2.92)
S'-M-O	91.49(5)	91.5(2) (N)	89.0(1)	91.45(8)	91.5	93.3(3)	92.8(4)	89.9(2)	90.9(4)	88.6(3) (N)	89.5(2) (N)	90.90(1.50)
S'-M-O'	169.50(4)	159.0(2) (N)	169.4(1)	161.43(8)	162.1	178.3(3)	174.6(4)	176.2(2)	161.2(4)	167.3(2) (N)	156.9(2) (N)	166.90(7.33)
N-M-N'	176.16(7)	177.5(2)	171.8(1)	172.4(1)	170.1	176.3(4)	176.1(5)	175.9(3)	159.9(5)	178.3(3)	169.0(2)	173.04(5.34)
N-M-O	83.40(6)	78.2(3) (N)	89.3(1)	81.1(1)	83.6	92.4(3)	89.4(4)	89.7(3)	86.8(5)	81.7(2) (N)	77.5(2) (N)	84.83(5.01)
N-M-O'	93.54(6)	100.5(2) (N)	94.6(1)	101.1(1)	89.6	88.9(3)	91.8(5)	93.3(3)	108.0(5)	97.6(2) (N)	91.4(2) (N)	95.49(5.79)
N'-M-O	93.92(6)	100.0(2) (N)	98.3(1)	91.3(1)	90.7	90.7(3)	94.3(4)	93.3(3)	109.8(5)	99.8(2) (N)	99.0(2) (N)	96.46(5.71)
N'-M-O'	83.58(6)	77.7(2) (N)	88.7(1)	79.5(1)	82.4	93.4(4)	93.4(5)	89.7(3)	85.6(5)	81.7(2) (N)	78.1(2) (N)	84.89(5.73)
O-M-O'	87.62(6)	90.3(2) (N)	88.4(1)	89.28(10)	91.5	85.9(3)	88.5(4)	86.4(3)	84.3(5)	89.2(2) (N)	89.7(2) (N)	88.28(2.09)

[a] This study.

TABLE 6. Comparison of bond lengths (Å) in bis-thiosemicarbazone metal complexes

Bond	Co[a]	Ni [19]	Cr [20]	Cr [16]	Cr [21]	Fe [22]	Fe [23]	Fe [17]	Fe [24]	Co [30]	Ni [18]	Average value
M-S1	2.204(1)	2.412(2)	2.407(1)	2.360(1)	2.31	2.274(3)	2.370(5)	2.234(3)	2.457(4)	2.230(1)	2.409(2)	2.333(90)
M-S'	2.202(1)	2.425(2)	2.4525(1)	2.385(1)	2.47	2.250(3)	2.318(6)	2.234(3)	2.429(5)	2.238(1)	2.440(2)	2.347(100)
M-N2	1.887(1)	2.026(5)	2.034(4)	2.012(3)	2.06	1.949(9)	1.979(12)	1.925(7)	2.124(11)	1.888(3)	2.056(6)	1.995(76)
M-N2'	1.883(1)	2.013(5)	2.041(4)	2.033(3)	2.03	1.960(9)	2.011(14)	1.925(7)	2.125(12)	1.874(3)	2.056(6)	1.995(77)
M-O	1.966(1)	2.114(6) (N)	1.947(3)	1.961(2)	1.94	1.952(7)	1.932(10)	1.946(6)	1.936(10)	1.922(3) (N)	2.106(7) (N)	1.948(14) [2.047(109) (N)]
M-O'	1.965(1)	2.110(6) (N)	1.927(3)	1.983(2)	2.17	1.905(8)	1.942(12)	1.946(6)	1.986(11)	1.926(3) (N)	2.125(7) (N)	1.978(82) [2.054(115) (N)]
S-C1	1.734(2)	1.735(6)	1.707(5)	1.717(4)	1.71	1.723(12)		1.750(9)	1.743(14)	1.731(4)	1.739(8)	1.745(43)
S'-C1'	1.734(2)	1.719(6)	1.719(6)	1.741(4)	1.84	1.723(12)		1.750(9)	1.775(17)	1.744(3)	1.724(8)	1.730(19)
C1-N1	1.331(2)	1.331(9)	1.336(6)	1.335(4)	1.31	1.299(14)		1.310(11)	1.337(20)	1.319(5)	1.308(10)	1.322(16)
C1'-N1'	1.334(2)	1.328(9)	1.344(6)	1.359(5)	1.32	1.390(14)		1.310(11)	1.262(21)	1.327(5)	1.326(11)	1.330(31)
C1-N3	1.341(2)	1.345(9)	1.311(6)	1.337(4)	1.27	1.398(14)		1.336(12)	1.344(21)	1.338(5)	1.352(9)	1.337(30)
C1'-N3'	1.338(2)	1.350(9)	1.307(7)	1.307(5)	1.37	1.390(14)		1.336(12)	1.370(21)	1.340(5)	1.335(10)	1.344(27)
N1-N2	1.385(2)	1.357(8)	1.393(6)	1.378(4)	1.39	1.398(11)		1.392(9)	1.393(18)	1.370(4)	1.370(8)	1.374(23)
N1'-N2'	1.375(2)	1.356(8)	1.388(8)	1.371(4)	1.38	1.444(12)		1.392(9)	1.412(18)	1.374(4)	1.342(8)	1.384(24)
N2-C2	1.292(2)	1.279(9)	1.307(6)	1.299(4)	1.36	1.277(15)		1.294(10)	1.281(19)	1.308(5)	1.260(10)	1.296(27)
N2'-C2'	1.290(2)	1.295(9)	1.288(5)	1.286(4)	1.37	1.292(13)		1.294(10)	1.281(19)	1.313(6)	1.285(11)	1.299(26)
C2-C3	1.504(2)	1.457(12)	1.422(6)	1.510(5)	1.48	1.429(17)			1.487(21)	1.443(6)	1.458(10)	1.462(32)
C2'-C3'	1.505(2)	1.446(12)	1.433(7)	1.523(5)	1.44	1.427(16)			1.456(22)	1.440(5)	1.445(11)	1.490(11)
C2-C4	1.487(2)			1.482(6)	1.28	1.405(16)			1.503(6)	1.503(6)		1.483(9)
C2'-C4'	1.484(2)			1.476(6)	1.33	1.366(15)			1.489(6)	1.489(6)		
C3-O1	1.288(2)	1.328(9) (N)	1.324(6)	1.286(4)	1.25	1.334(13)			1.320(16)	1.311(5) (N)	1.324(6)	1.304(30) [1.320(12) (N)]
C3'-O1'	1.292(2)	1.318(9) (N)	1.332(6)	1.287(4)	1.30	1.313(12)			1.307(20)	1.294(5) (N)	1.332(6)	1.309(15) [1.306(17) (N)]
C3-O2	1.229(2)		1.228(4)									
C3'-O2'	1.236(2)		1.220(4)									

[a] This study.

within the range reported for other octahedral Co(III) compounds of thiosemicarbazones and related ligands [33].

Electrochemical studies

The $H_2PVATSC$ ligand exhibits two irreversible reduction peaks at -0.35 (peak A) and -1.20 (peak B) V, with the latter peak probably corresponding to reduction of the conjugated portion of the thiosemicarbazide chain and its value comparable with that observed [34] for other thiosemicarbazone ligands (-1.31 V at pH 6.0) and the former peak corresponding to a reduction process probably coupled to peak B.

The monomeric thiolato Co(III) complex undergoes reversible metal based one-electron reduction at -0.90 V. Other cobalt compounds containing mixed thionethiol tautomers also exhibit metal based reductions in a similar range [35] although these potentials are on the high side compared with the corresponding iron(III) compounds. This is perhaps indicative of an enhanced stabilization of the trivalent cobalt ion by these ligands. The second irreversible peak at -1.22 V for the cobalt complex corresponds to the reduction of the coordinated azomethine linkage. For the present compounds this peak is shifted in the negative direction upon complexation, whereas for the thione or mixed thione–thiol species it is shifted to the positive side. This suggests that thiol coordination stabilizes the trivalent oxidation state of the metal.

The present results indicate that complexation of an electrochemically active metal ion to thiosemicarbazide ligands can thus provide a marker for predicting and modulating their biological activities.

Conclusions

Pyruvic acid thiosemicarbazone coordinates in its binegative form to the central cobalt(III) atom forming a six-coordinate complex. Due to the arrangement of the two ligands a *meridional* isomer is formed with *cis* sulfur, *trans* nitrogen and *cis* oxygen donor atoms. The two five-membered rings formed by each ligand are puckered towards each other resulting in a distortion from regular octahedral geometry about the cobalt atom. The ligand $H_2PVATSC$ undergoes irreversible reduction of the azomethine group at -1.20 V. The cobalt complex undergoes reversible metal based one-electron reduction at -0.90 V.

Acknowledgements

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