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The X-Ray Crystal Structure of Bis(N-sulphinylphenylhydrazino)cobalt(II), Crystallized as a Pyridine Adduct

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Infrared spectroscopy indicates and X-ray crystallography confirms that the deprotonated N-sulphinylphenylhydrazine ligands are chelated in the complex $Co(PhNNSO)_2py_2$, which is the first example of coordination of a transition metal via the oxygen atom of the N=S=O moiety.

Co-ordination of the N=S=O group via the sulphur atom has been proposed for the reaction [1] of $Ir(PPH_3)(CO)Cl$ with 4-nitro-N-sulphinylaniline and for [2] $RhCl(P\text{-}1\text{-}Pr_3)(4\text{-}MeC_6H_4NSO)$; a side-on co-ordination [3] via the =N=S Bond has been established for $Pt(PPh_3)_2PhNSO$ and analogous Ni(0) complexes [4]. The infrared spectra of deprotonated N-sulphinylphenylhydrazine complexes [5] of copper and nickel(II) indicated that the PhN^1N^2SO anion was chelated to the metal via N^1 and the oxygen atom of the N=S=O group. The lack of crystalline products precluded X-ray analysis of these compounds.

However, we have obtained crystals of bis(N-sulphinylphenylhydrazino)bispyridinecobalt(II) by the reaction of cobalt(II) acetate in ethanolic solution with N-sulphinylphenylhydrazine and pyridine. Of composition $Co(PhNNSO)_2py_2$, the blue crystals exhibit paramagnetic behaviour at 298 K (μ_{eff} = 4.60 B.M.), indicating a high-spin octahedral configuration in a fairly symmetrical ligand field. The infrared spectrum shows that deprotonation of the N-sulphinylphenylhydrazine ligand has occurred. In addition, the S=O stretching mode of PhNNSO has shifted from 1155 cm^{-1} to 953 cm^{-1} and the N=S stretching mode from 1270 to 1279 cm^{-1}.

If PhNN=S=O and PhNN=$\overset{+}{S}$–$\bar{O}$ are considered as contributing canonical structures of the ligand, donation through oxygen would result in a lowering in wavenumber of the S–O stretching mode whilst donation through sulphur would increase the S–O stretching vibration. These experimental wavenumber shifts indicate that the N–S–O moiety is bonded to the metal via the oxygen atom. This has been confirmed by the X-ray crystal structure shown in Fig. 1.

Crystal Data

$C_{22}H_{22}N_6O_2S_2Co$, M = 525.51, triclinic, space group $P\bar{1}$, a = 8.941(2), b = 13.116(3), c = 15.958(4) Å, α = 78.24(2), β = 83.69(2), γ = 72.77(2)°, V = 1747(8) Å^3, Z = 3, D_c = 1.50 g cm^{-3}, $F(000)$ = 813 electrons, $\mu(MoK_\alpha)$ = 9.0 cm^{-1}. Intensity data in the range $2 < 2\theta < 45°$ were recorded at 298 K on a Syntex $P2_1$ diffractometer using graphitemonochromated MoK_α radiation (λ = 0.71069 Å) and a fixed speed of 3° min^{-1} in the $2\theta - \omega$ mode; 2292 reflections out of 4588 had $F > 3\sigma(F)$. The structure was solved by direct methods (MULTAN 80) and refined to the current R_w ($w = 1/\sigma^2$) of 0.0552 using the program package SHELX-76 and anisotropic temperature factors for Co and S; the phenyl and pyridine groups were refined as idealized rigid groups but with individual temperature factors for each atom.

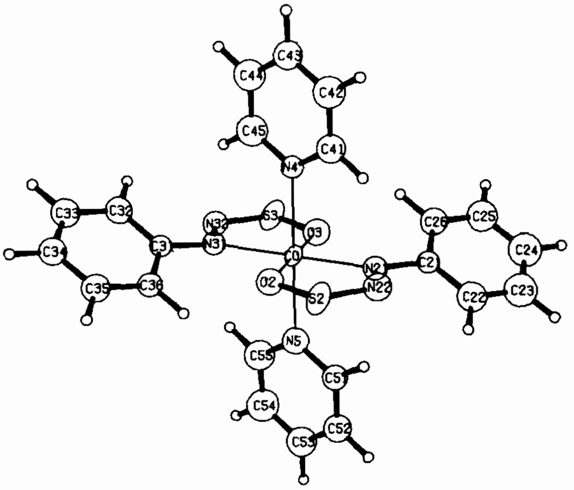

Fig. 1. The coordination about Co2. The case of Co1 is not depicted but important bond and angle values are given below in parentheses after the corresponding data for Co1. Distances: Co–O2 2.045(2.034), Co–O3 2.056(2.034), Co–N21 2.165(2.180), Co–N31 2.179(2.180), Co–N4 2.228(2.206), Co–N5 2.231(2.206), S2–O2 1.528(1.528), S2–N22 1.602(1.596), S3–O3 1.533(1.528), S3–N32 1.608(1.596), N21–N22 1.282(1.313), N21–C21 1.447 (1.427), N31–N32 1.298(1.313), N31–C31 1.392(1.427), Angles: N4–Co–N5 179.5(180), N31–Co–N21 179.9(180), O2–Co–O3 179.0(180), Co–O2–S2 116.0(114.8), Co–O3–S3 116.0(116.0), O2–S2–N22 109.8(110.5), O3–S3–N32 109.3(110.5), S2–N22–N21 116.5(116.1), S3–N32–N31 117.7(116.1), N22–N21–C21 112.7(111.2), N32–N31–C31 113.6(111.2), e.s.d.s are 0.007–0.015 Å and 0.3–0.9° for the distances and angles, respectively.

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TABLE I. Distances in $C_{22}H_{22}N_6O_2S_2CO$.

	Dist. (Å)	S.D. (Å)
Co1–2O1	2.034	0.008
Co1–2N11	2.180	0.010
Co1–2N6	2.206	0.008
Co2–O2	2.045	0.008
Co2–O3	2.056	0.009
Co2–N21	2.165	0.011
Co2–N31	2.179	0.010
Co2–N4	2.228	0.009
Co2–N5	2.231	0.007
S1–O1	1.528	0.009
S1–N12	1.596	0.010
S2–O2	1.528	0.009
S2–N22	1.602	0.012
S3–O3	1.533	0.010
S3–N32	1.608	0.012
N11–N12	1.313	0.014
N11–C11	1.427	0.011
N12–N11	1.313	0.014
N12–S1	1.596	0.010
N21–N22	1.282	0.014
N21–C21	1.447	0.014
N22–N21	1.282	0.014
N22–S2	1.602	0.012
N31–N32	1.298	0.015
N31–C31	1.392	0.012
N32–N31	1.298	0.015
N32–S3	1.608	0.012
O1–S1	1.528	0.009
O2–S2	1.528	0.009
O3–S3	1.533	0.010
C11–N11	1.427	0.011
C21–N21	1.447	0.014
C31–N31	1.392	0.012

The structure contains two crystallographically different cobalt atoms. In both cases the coordination by the N-sulphinylphenylhydrazine ligands and the pyridine solvent molecules is the same: two ligands form bonds to cobalt through their oxygen and nitrogen donor atoms while two pyridine ligands at *trans*-positions complete the coordination octahedron (Fig. 1). In the case of Co2 the ligands and the solvent molecules are symmetry-related (Co2 at 0, 0, 0).

The Co–O and Co–N bond lengths (see Table I) appear normal for octahedrally coordinated Co(II), *cf.* ref. 6. On co-ordination, the NSO and the NNS angles of the N-sulphinylphenylhydrazine ligand have decreased slightly; sp^3 hybridization at the sulphur atom is indicated. The sulphur–oxygen bond length, as compared to the free ligand [7], has increased by 0.06 Å, which represents a considerable decrease in the multiple-bond character of the sulphur–oxygen linkage due to coordination; the mean value of the S–O distance found here (1.529 Å) may be compared with that of 1.557(4) Å in the O-bonded dimethyl sulphoxide ligand [8] found in dichlorotetrakis(dimethylsulphoxide)ruthenium(II); in this compound, the sulphur–oxygen stretching mode [9] is found at 915 cm^{-1}. This vibrational mode together with its associated bond lengths indicates that the sulphur–oxygen bond in the O-bonded dimethylsulphoxide ligand in dichlorotetrakis(dimethylsulphoxide)ruthenium(II) has a somewhat greater single bond character than the sulphur–oxygen bonds in bis(N-sulphinylphenylhydrazino)-bispyridinecobalt(II).

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