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THE X-RAY ANALYSIS OF BIS(1-(2-THIAZOLYLAZO)-2-NAPHTHOLATO)-COBALT(III) PERCHLORATE

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Crystal structure of bis(1-(2-thiazolylazo)-2-naphtholato)cobalt(III) perchlorate was determined by X-ray analysis. A cobalt atom is surrounded octahedrally by two terdentate ligands in the mer configuration. Short intramolecular contacts of 2.2-2.3 Å are observed between azo nitrogen atom(N(2)) and naphthol hydrogen atom(H(9)).

1-(2-Thiazolylazo)-2-naphthol(abbreviated as H-TAN), $C_{13}H_9N_3OS$, forms colored complexes with various metals, and therefore it has been used as an analytical reagent. The structures of Fe(II)-,[1] Ni(II)-,[2] Cu(II)-,[3] and Pd(II)-TAN[4] complexes have been reported; however, that of a Co(III)-TAN complex is still unknown and two different structures have been proposed.[5,6] In order to establish the structure of the TAN-complex with a trivalent matal and to obtain some structural details, an X-ray determination of bis(1-(2-thiazolylazo)-2-naphtholato)cobalt(III) perchlorate($[Co^{III}(TAN)_2]\cdot ClO_4$) has been undertaken.

Single crystals of $[Co^{III}(TAN)_2]\cdot ClO_4$ were grown from an ethanol solution by slow evaporation. The crystal data are: $[Co^{III}(C_{13}H_8N_3OS)_2]\cdot ClO_4$, F.W. 667.0; monoclinic, a=10.348(2), b=21.066(5), c=13.072(5) Å, β=112.35(3)°, V=2635.4 Å^3; Z=4, D_m=1.67, D_x=1.68 g/cm^3; μ=9.9 cm^{-1}(for MoKα); space group $P2_1/c$. The intensities of unique reflections with 2θ values less than 55° were collected on a Rigaku automated four-circle diffractometer using MoKα radiation. A total of 2690 independent reflections with $|F| > 3\sigma(F)$ were obtained. The data were corrected for Lorentz and polarization effects, but no corrections were made for absorption and extinction.

The structure was solved by the heavy-atom method. Fourier synthesis of electron density phased on the positions of a cobalt and two sulfur atoms revealed the location of the remaining atoms except hydrogen atoms. A difference synthesis showed the positions of all but one hydrogen atoms, the remaining hydrogen position being evaluated by calculation. The structure was refined by the least-squares procedure, with anisotropic and isotropic temperature factors for non-hydrogen and hydrogen atoms, respectively, and the final R value was reduced to 0.051 for the 2690 observed reflections.

The crystal is composed of $[Co^{III}(TAN)_2]^+$ cation and ClO_4^- anion. The thermal ellipsoids of atoms are given in Fig. 1. The complex cation has approximately C_2 symmetry, and the cobalt atom is surrounded octahedrally by two ligand anions(referred to as A and B) in the mer configuration. The TAN acts as a terdentate ligand, being coordinated to the metal through the phenolic oxygen atom, the azo nitrogen atom adjacent to the naphthol ring and the thiazole nitrogen atom, to give two five-membered chelate rings. Such mode of coordination is observed in the Fe(II)-, Ni(II)-, Cu(II)- and Pd(II)-TAN complexes. It is to be noted that the participation of the thiazole sulfur atom in metal binding has never been reported in metal-TAN complexes.

The geometries of the two moieties agree well within the limit of three times their corresponding e.s.d.'s, the average distances and angles being shown in Fig. 2. The average Co-O distance of 1.888(4) Å is in agreement with accepted values. All the Co-N distances, especially Co-N(1) and Co-N(1') are shorter than the value observed in $[Co^{III}(NH_3)_6]^{3+}$ complex(1.972(1) Å).$^{7)}$ The bond angles around the metal, O-Co-N(1) and N(1)-Co-N(3) are compressed to 84.9(2) and 81.6(2)°, respectively. On the other hand, N(2)-N(1)-C(1), N(1)-C(1)-C(10), N(2)-C(11)-S and Co-N(3)-C(13) are enlarged to 126.0(5), 128.1(5), 124.5(5) and 139.1(4)°, respectively. These are the characteristic features usually observed in the metal-TAN complexes.

The N(1)-N(2) distance of 1.301(7) Å lies between the standard single-bond distance (1.44 Å of >N-N< in hydrazine, or 1.38 Å of =N-NH- in hydrazone compounds) and the standard double-bond distance(1.24 Å of -N=N- in azobenzene analogues). These findings are indicative of the presence of some delocalization of π-electrons in the azo group. Similarly, C(1)-N(1) and C(2)-O distances of 1.349(8) and 1.291(8) Å respectively are between the corresponding standard values of single and double bonds.

Inspection of a molecular model reveals that short contact would appear between N(2) and H(9)(hydrogen atom attached to C(9)). If the chelation does not affect the bond lengths and angles of the ligand anion, the N(2)···H(9) distance will be less than 1.80 Å. The observed distances are 2.24(6) Å for A and 2.28(6) Å for B. The bond angle distribution mentioned above indicates that the ligand anion deforms so as to make the N(2)···H(9) distance longer on the chelate ring formation. Both of the ligand

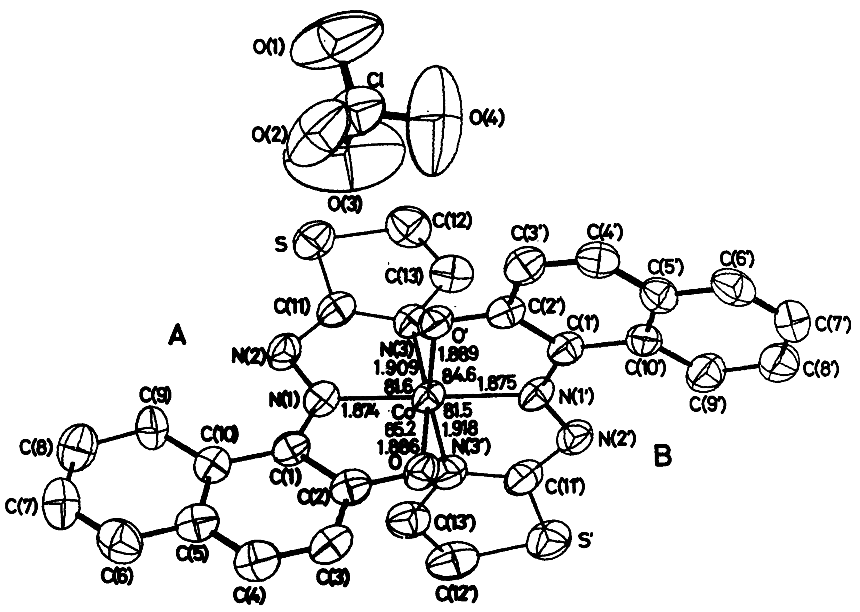

Fig. 1 Thermal ellipsoids of atoms

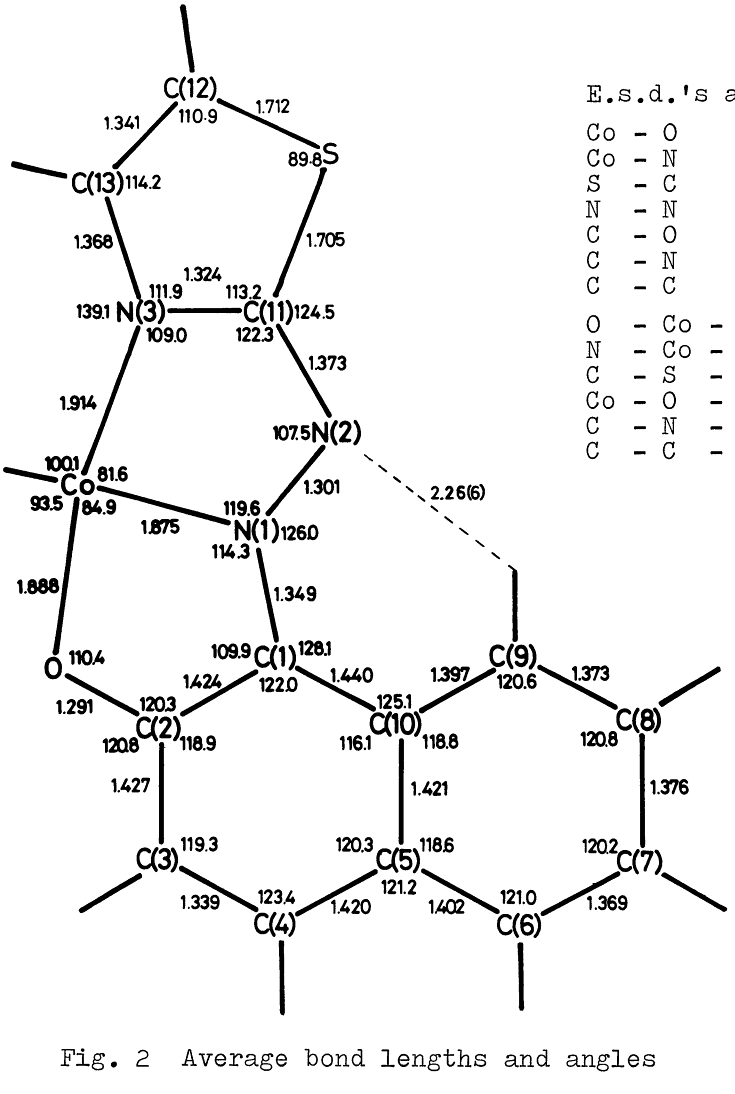

Fig. 2 Average bond lengths and angles

E.s.d.'s are:

Co - O	0.004 Å
Co - N	0.005 - 0.006 Å
S - C	0.007 - 0.008 Å
N - N	0.007 Å
C - O	0.008 Å
C - N	0.008 - 0.009 Å
C - C	0.009 - 0.012 Å
O - Co - N	0.2°
N - Co - N	0.2°
C - S - C	0.4°
Co - O - C	0.4°
C - N - N	0.5°
C - C - C	0.6 - 0.8°

anions are significantly deviated from planarity(maximum deviation: 0.08 Å for A and 0.17 Å for B). However, both of naphthalene rings are planar within the deviation of ±0.02 Å; in A and B, N(2) and C(9) are displaced from the naphthalene plane on opposite sides. This may indicate the steric hindrance between N(2) and H(9) atoms.

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