Crystal and Molecular Structure of the High-spin Five-co-ordinate Complex Aquo-*NN'*-ethylenebis-(3-methoxysalicylideneiminato)cobalt(II)

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray data by conventional Fourier methods. Crystals are orthorhombic, space group *Pnma*, with $Z = 4$ and cell parameters $a = 8{\cdot}98$, $b = 24{\cdot}95$, $c = 7{\cdot}72$ Å. A least-squares refinement, based on 365 independent reflexions, reduced *R* to 0·058. The crystals consist of five-co-ordinate molecules in an umbrella shape, held together by van der Waals forces and hydrogen bonds. The cobalt atom is displaced 0·43 Å from the basal plane towards the apical water molecule [Co–O 2·12(2) Å]. The basal Co–O and Co–N bond lengths [1·95(1) and 2·05(1) Å] are significantly greater than those found in analogous low-spin complexes. Such structural results may be indicative of a smaller metal–ligand π-bonding contribution in high-spin quadridentate Schiff-base complexes as compared with the low-spin species.

FIVE-CO-ORDINATE cobalt(II) complexes with quadridentate Schiff bases have been found to exist in a low- or high-spin state depending on the nature of the co-ordinated ligands.[1] Recent *X*-ray results [2-4] have shown that the low-spin species are characterized by a square pyramidal geometry, although steric effects can produce a distortion towards a trigonal bipyramidal arrangement.[4] However, no structural data are available for high-spin complexes in order to allow a comparison between the stereochemistries of the two paramagnetic species.

It has been shown [5,6] that the spin state of the cobalt(II) atom, in five-co-ordinate complexes, is related to the nucleophilicity n^0 of the donor atoms as well as to the structural parameters of the co-ordination polyhedron of the metal atom. Since n^0 is determined by the polarizability and π-bonding properties of the ligands, useful information about the nature of the metal–ligand bonds may be gained from a knowledge of the molecular structure. As part of a general investigation of the structural aspects of metal complexes with quadridentate Schiff bases we report here the crystal and molecular structure of the high-spin complex [1] aquo-*NN'*-ethylenebis-(3-methoxysalicylideneiminato)cobalt(II), hereinafter [Co(3-MeOsalen)(H_2O)], for which a five-co-ordinate structure is expected.[7]

EXPERIMENTAL

Red single crystals were obtained by slow evaporation of a hot saturated acetonitrile solution.

Crystal Data.—$C_{18}H_{20}CoN_2O_5$, $M = 403{\cdot}3$, Orthorhombic, $a = 8{\cdot}98$, $b = 24{\cdot}95$, $c = 7{\cdot}72$ Å, $U = 1729{\cdot}7$ Å^3, D_m (by flotation) $= 1{\cdot}52$, $Z = 4$, $D_c = 1{\cdot}54$, $F(000) = 836$. Space group *Pnma* (D_{2h}^{16}) from structure analysis. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 10{\cdot}7$ cm^{-1}.

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined by use of an on-line automated Siemens diffractometer with Mo-K_α radiation.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan technique and Mo-K_α radiation. Because of the small size of the available crystals only 365 independent reflexions were significantly above the scattering background [$I_0 > 3\sigma(I_0)$] in a maximum θ angle of about 25°. Correction for the Lorentz-polarization factor was applied. No correction for extinction, absorption (μR *ca.* 0·07), or anomalous dispersion of the cobalt atom was made.

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods assuming the centrosymmetric space group *Pnma* instead of the non-centrosymmetric $Pna2_1$ (a non-standard setting of $Pna2_1$, No. 33). The choice was suggested by the Co ··· Co vector distribution on the three-dimensional Patterson map and confirmed by the subsequent successful refinement. Furthermore a preliminary block-diagonal matrix least-squares refinement carried out in $Pna2_1$ led to an *R* value significantly larger than that obtained in *Pnma*. The electron-density map suggested a statistical occupancy of the carbon atoms of the ethylene bridge. This was confirmed by the large value of the temperature factor (*B* 7·8 Å^2) of the crystallographically independent carbon atom after an isotropic least-squares refinement and the very short value of the CH_2–CH_2 distance (1·38 Å).

Thus the carbon atom was located in two positions with an occupancy factor 0·5. Because of the small number of available reflexions, no attempt was made to locate the hydrogen atoms and only the Co, O, and N atoms were refined anisotropically. The final block-diagonal matrix least-squares refinement reduced *R* to 0·058. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 20$, $B = 1{\cdot}0$, and $C = 0{\cdot}0071$, chosen in order to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$. Final atomic parameters are

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[1] (*a*) M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.*, 1946, **68**, 2267; (*b*) A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1968, 241; (*c*) L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, 1972, **11**, 457.

[2] (*a*) S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671; (*b*) R. de Iasi, B. Post, and S. L. Holt, *Inorg. Chem.*, 1971, **10**, 1498.

[3] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[4] N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 498.

[5] P. L. Orioli, *Co-ordination Chem. Rev.*, 1971, **6**, 285.

[6] L. Sacconi, *Co-ordination Chem. Rev.*, 1972, **8**, 351.

[7] Presented in part at the Italo-Yugoslav Meeting of Crystallography, Trieste, 1973, Abstracts, p. 202.

listed in Table 1 together with their estimated standard deviations, calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. The numbering scheme of the atoms is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21006 (3 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 8. Bond lengths and angles with their estimated standard deviations are in Table 2, intermolecular distances <3·8 Å in Table 3.

TABLE 1

Fractional co-ordinates (× 10^4) and thermal factors * with estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	605(3)	2500(0)	590(5)	64(3)	0	−31(14)	9·8(4)	0	220(6)
O(1)	2106(10)	1937(3)	638(18)	94(12)	16(8)	−46(43)	10(1)	−54(15)	271(24)
O(2)	4527(12)	1345(4)	958(18)	113(13)	15(11)	−116(42)	15(2)	−30(13)	289(29)
O(3)	−347(15)	2500(0)	3104(19)	80(20)	0	124(49)	13(2)	0	183(34)
N	−830(12)	1980(5)	−608(24)	83(17)	37(10)	−148(62)	19(2)	−77(20)	392(36)

				B/Å²					B/Å²
C(1)	2024(16)	1423(6)	111(19)	3·5(3)	C(6)	777(16)	1193(6)	−601(22)	3·0(3)
C(2)	3271(16)	1095(5)	289(22)	3·3(3)	C(7)	−653(21)	1480(7)	−1018(21)	4·8(4)
C(3)	3263(17)	538(6)	−75(21)	3·9(4)	C(8)	5897(20)	1049(7)	1066(22)	4·9(4)
C(4)	1965(20)	335(7)	−775(27)	5·7(4)	C(9)	−2359(33)	2176(11)	−766(47)	2·7(6)
C(5)	715(21)	632(7)	−1078(22)	5·3(4)	C(10)	−2069(37)	2699(11)	−1746(46)	3·9(9)

* The anisotropic temperature factors (× 10^4) are in the form: exp− $(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)$.

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Co–O(1)	1·95(1)	N–C(10)	1·63(4)
Co–O(3)	2·12(2)	C(1)–C(2)	1·39(2)
Co–N	2·05(1)	C(2)–C(3)	1·42(2)
O(1)–C(1)	1·35(2)	C(3)–C(4)	1·38(2)
O(2)–C(2)	1·39(2)	C(4)–C(5)	1·37(3)
O(2)–C(8)	1·44(2)	C(5)–C(6)	1·45(2)
N–C(7)	1·30(2)	C(6)–C(7)	1·51(2)
N–C(9)	1·46(3)	C(9)–C(10)	1·53(4)

(*b*) Angles

O(1)–Co–O(1′)	92·3(4)	O(1)–C(1)–C(6)	124(1)
O(1)–Co–O(3)	105·2(5)	C(2)–C(1)–C(6)	117(1)
O(1)–Co–N	89·3(4)	O(2)–C(2)–C(1)	115(1)
O(1)–Co–N′	154·2(7)	O(2)–C(2)–C(3)	121(1)
O(3)–Co–N	99·2(6)	C(1)–C(2)–C(3)	124(1)
Co–O(1)–C(1)	130·0(9)	C(2)–C(3)–C(4)	116(1)
C(2)–O(2)–C(8)	119(1)	C(3)–C(4)–C(5)	124(2)
Co–N–C(7)	130(1)	C(4)–C(5)–C(6)	117(2)
Co–N–C(9)	115(1)	C(1)–C(6)–C(5)	123(1)
Co–N–C(10)	111(1)	C(1)–C(6)–C(7)	126(1)
C(7)–N–C(9)	115(2)	C(5)–C(6)–C(7)	112(1)
C(7)–N–C(10)	115(2)	N–C(7)–C(6)	121(2)
O(1)–C(1)–C(2)	119(1)	N–C(9)–C(10′)	100(2)

Calculations.—All calculations were carried out on a CDC 6200 computer, with programs described in ref. 9. A local program was used to obtain best molecular planes, whose equations were calculated according to ref. 10.

RESULTS

The Structure.—The results confirm the five-co-ordinate structure of the title compound. The co-ordination polyhedron of the cobalt atom is a distorted square pyramid, the basal plane being defined by the oxygen and nitrogen atoms of the quadridentate Schiff base. The cobalt atom is displaced 0·43 Å from this plane towards the water molecule in the apical position. The overall geometry of the molecule (Figure 2) is very similar to that of other

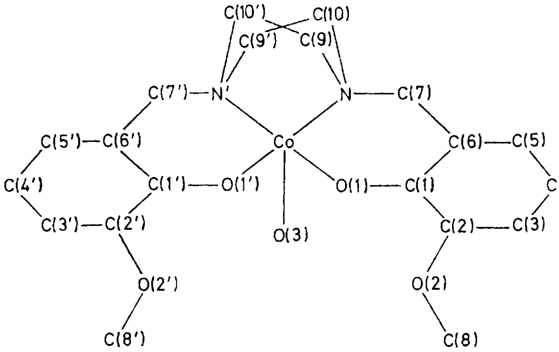

FIGURE 1 Numbering scheme of the atoms. Primed atoms are related by a crystallographic mirror plane

TABLE 3

Intermolecular distances (Å) <3·8

Co ··· O(3^{I})	3·77(1)	Co ··· C(10^{II})	3·66(4)
O(1) ··· O(3^{I})	2·85(2)	O(1) ··· C(10^{II})	3·63(4)
O(2) ··· O(3^{I})	2·97(1)	C(1) ··· C(7^{II})	3·79(2)
O(2) ··· C(1^{I})	3·78(2)	C(2) ··· C(7^{II})	3·57(2)
O(2) ··· C(6^{I})	3·78(2)	C(3) ··· C(5^{II})	3·71(2)
O(3) ··· C(9^{I})	3·48(4)	C(2) ··· C(9^{III})	3·73(3)
C(8) ··· O(1^{I})	3·54(2)	C(8) ··· C(7^{III})	3·65(3)
C(8) ··· C(1^{I})	3·26(2)	C(8) ··· C(9^{III})	3·52(3)
C(8) ··· C(2^{I})	3·53(2)	C(4) ··· C(5^{V})	3·70(3)
C(8) ··· C(6^{I})	3·52(2)	C(5) ··· C(5^{V})	3·79(3)

The superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $\frac{1}{2} + x, y, \frac{1}{2} - z$
III $1 + x, y, z$
II $\frac{1}{2} + x, y, -\frac{1}{2} - z$
IV $-x, -y, -z$

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. C. S.* (*Dalton*), 1973, Index issue, items less than 10 pp. are supplied as full size copies.

[8] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[9] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

[10] V. Schomaker, J. Waser, R. F. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

five-co-ordinate salen complexes such as [Co(salen)(py)] (ref. 3) and [Co(salbn)(py)] (ref. 4) resembling a 'reversed umbrella.' In fact, because of the crystallographic mirror symmetry, the four in-plane donor atoms are exactly coplanar and their plane makes a dihedral angle of *ca.* 13° with that of the crystallographically independent 3-methoxysalicylaldimine residue [planar to within ±0·07 Å, neglecting C(8)]. The methyl carbon atom C(8) is only slightly displaced (0·12 Å) from this plane on the opposite side from the water molecule making a close contact [2·83(2) Å] with C(3). Thus the two halves of the quadridentate ligand are bent 26° away from the water molecule. The carbon atoms of the ethylene bridge are 'disordered' so as to maintain a statistical mirror symmetry for the whole complex, the positions obtained by the least-squares refinement corresponding to a nearly *gauche* conformation (torsion angle *ca.* 53°). In the other five-co-ordinate complexes so far examined by *X*-ray analysis, the torsion angle around the C–C bond has been found to be more or less zero. However it is sometimes doubtful whether such a geometry is actual or is the result of 'disordered' *gauche* conformations. In fact the *cis*-conformation is observed, in these cases, when the ethylene-bridge carbon atoms have large thermal factors.

Bond lengths and angles in the quadridentate ligand are similar to those found in other complexes of this type.[11] Values for the methoxy-group are also as expected. However, a significant difference is found between the co-ordination parameters for this complex and those for its low-spin analogues. In fact the Co–O and Co–N bond lengths change from the average values of 1·904(6) and 1·912(12) Å to 1·95(1) and 2·05(1) Å. As a consequence of the Co–N distance lengthening, the N–Co–N bond angle is reduced from the usual value of *ca.* 86°, found in low-spin species, to 78·6° since the N–N bite has to be maintained constant (*ca.* 2·58 Å) for the five-membered ring closure.

The molecules are held together by van der Waals forces and hydrogen bonds (see Table 3), the latter involving the water molecule of one unit and the metal co-ordinating oxygen atoms of another unit [O···O, 2·85(2) Å, O···O–Co, 129°]. The resulting crystal packing (Figure 2) is very close, and particularly efficient in pairs.

DISCUSSION

In Table 4 some data are reported for cobalt(II) five-co-ordinate complexes with salen-type ligands whose structure has been determined by *X*-ray methods. The most remarkable feature is the similarity among the structural parameters of the low-spin species, which are quite different from those of the present high-spin complex, values for which are characteristic of square-pyramidal high-spin complexes.[5,6] Thus the main differences between low- and high-spin complexes are the lengthening of the basal Co–O(N) distances and a more marked out-of-plane displacement of the metal atom in the latter species. Furthermore it may be seen, as already pointed out by Sacconi,[6] that high-spin pyramidal complexes are characterized by apical angles, α, of *ca.* 100° whereas in the low-spin derivatives a distortion occurs towards 90°. However, such an effect is fully evident and significant only for ligands which are similar in their steric and electronic effects. The spin state of the cobalt atom depends upon the nature of the four-co-ordinate Schiff base, so that [Co(salen)(py)] is low-spin whereas [Co(3-MeOsalen)(py)] (ref. 12) is high-spin (μ_{eff} 3·70 B.M.). It has been suggested [6] that the spin state in five-co-ordinate complexes may be related to the overall nucleophilicity, Σn^0, or to the overall electronegativity, $\Sigma\chi$, of the five donor atoms. However such criteria fail in the cases in which a distortion from the typical geometry in observed, probably because of π-bonding contributions.[6] The $\Sigma\chi$ and Σn^0 values of the present complex (Table 4) are as expected for a high-spin complex. On the other hand the same values apply to the low-spin species [Co(salen)]$_2$, although in the latter a greater π-bonding contribution is to be expected. In fact it has been shown that low-spin cobalt complexes with quadridentate salen-type ligands have a somewhat extended

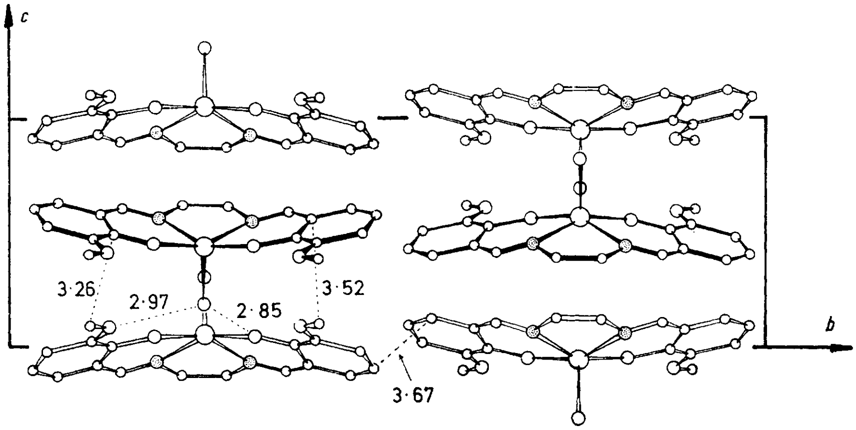

FIGURE 2 A projection of the cell contents down the *a* axis. For sake of clarity the ethylenediamine bridge is sketched in the *cis*-conformation

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[11] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

[12] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.

π-conjugation which also involves the cobalt atom.[11,13] The foregoing hypothesis is supported by the structural parameters. In fact coplanarity of the cobalt atom with the basal donor atoms would make π-bonding more efficient, as already suggested by Furlani.[14] However, such an effect is opposed by the σ-bond formation with the apical ligand, which tends to withdraw the metal atom out of the basal plane so as to increase σ-orbital overlap. The increase in the distance, *d*, may therefore be indicative of a decrease of the π-bonding contribution in the metal to equatorial ligand bonds. This should be reflected in a different electron situation of the metal atom and therefore in its chemical behaviour, such as redox properties.[13,15] In this respect it is interesting to observe that salen-type cobalt(II) complexes with higher magnetic moments react with organic halides by an ' outer-sphere ' electron-transfer mechanism instead of by halogen abstraction, as preferred by the low-spin compounds.[1c] It seems likely that such a difference is related to the different nature of the co-ordination bonds, as discussed earlier, which results in a lesser ' electron availability ' on the metal atom in the low-spin species.

TABLE 4

Some characteristic data for five-co-ordinate salen-type complexes

	[Co(salen) (py)] [a]	[Co(salbn) (py)] [b]	[Co(salen)]$_2$ [c]	[Co(3-MeOsalen)(H$_2$O)] [d]
$\Sigma\chi$	16·21	16·21	16·64	16·64
Σn^0 [e]	14·10	14·10	13·40	13·40
$\mu_{eff.}$/B.M. [f]	2·23	*g*	2·18	4·25
Co–O(basal)/Å	1·90(1)	1·906(7)	1·901(4)	1·95(1)
Co–N(basal)/Å	1·90(1)	1·87(1)	1·907(5)	2·05(1)
Co–O(apical)/Å			2·259(4)	2·12(1)
Co–N(apical)/Å	2·10(2)	2·14(1)		
d/Å [h]	0·20	0·21	0·15	0·43
α/° [i]	93·4(5)—98·4(6)	94·1(3)—100·9(4)	84·9(3)—101·7(4)	99·2(6)—105·2(5)

[a] From ref. 3. [b] From ref. 4; salbn = *NN'*-butylenebis(salicylideneiminato) dianion. [c] From ref. 2(*b*). [d] From present work. [e] From ref. 6. [f] From ref. 1(*b*). [g] Not known. [h] Displacement of the cobalt atom from the basal plane. [i] Range of the co-ordination angles involving the apical ligand.

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[14] C. Furlani, *Co-ordination Chem. Rev.*, 1968, **3**, 141.

[15] G. Costa, A. Puxeddu, and E. Reisenhofer, to be published. These authors have shown that the reduction process of the 3-MeOsalen complex is irreversible in contrast with the behaviour of the low-spin analogues.