Crystal and Molecular Structure of [*NN'*-ethylenebis(salicylideneiminato)]pyridine(vinyl)cobalt(III). Evidence of *trans*- and *cis*-Influence in Octahedral Complexes

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray data by conventional Fourier methods. The crystals are orthorhombic, space group *Pnma*, with $Z = 4$, and cell dimensions $a = 15{\cdot}902(5)$, $b = 17{\cdot}871(10)$, $c = 6{\cdot}746(4)$ Å. After an anisotropic block-diagonal least-squares refinement *R* was 0·070 for 917 reflections. The cobalt atom has a distorted octahedral co-ordination polyhedron. The ' salen ' ligand occupies the four equatorial positions whereas the vinyl group and the pyridine molecule occupy the two axial positions [Co–C 1·93(2) and Co–N 2·12(1) Å]. The complex has an umbrella-shape conformation with apparent *m* symmetry because of the statistical disorder of the vinyl group and ethylene bridge in the mirror plane. Comparison of the cobalt–axial-ligand bond lengths with those of analogous compounds provides further evidence of *trans*- and *cis*-influence in such octahedral complexes.

THE three aspects of the *trans*-effect of a ligand in octahedral complexes, *i.e.* kinetic, thermodynamic, and ground-state, have been widely studied.[1] Recently an increasing amount of experimental data has been reported on the last two aspects, because they can be more simply rationalised, and the simple electronic model, which has been suggested to explain the *trans*-influence in square planar [2] complexes, has been extended to octahedral complexes.[3]

The octahedral cobalt complexes having as equatorial ligands quadridentate Schiff bases like bae † and salen ‡ revealed themselves a suitable system to study *trans*- and *cis*-influence because it is possible to obtain series of strictly related compounds, where more reliable comparisons can be carried out.

Recently we have reported evidence of *trans*-influence in this type of complex.[4]

The results of the structure of [*NN'*-ethylenebis-(salicylideneiminato)]pyridine(vinyl)cobalt(III) determination, related to those previously reported, give further evidence of *trans*-influence. Furthermore, the analysis of the structural data of this and analogous compounds suggests the possibility of *cis*-influence of the different quadridentate ligands on the axial bonds.

EXPERIMENTAL

Crystal Data.—$C_{23}H_{22}CoN_3O_2$, $M = 431{\cdot}4$, Orthorhombic, $a = 15{\cdot}902 \pm 0{\cdot}005$, $b = 17{\cdot}871 \pm 0{\cdot}010$, $c = 6{\cdot}746 \pm 0{\cdot}004$ Å, $U = 1916{\cdot}8$ Å^3, $D_m = 1{\cdot}50$, $Z = 4$, $D_c = 1{\cdot}495$, $F(000) = 896$. Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-$K_{\bar{\alpha}}$) = 17·8 cm^{-1}. Space group *Pnma* (D_{2h}^{16}) from structure determination. Cell parameters were determined from precession photographs and after alignment of the crystal on a Hilger and Watts four-circle diffractometer, were refined by the least-squares method of Busing and Levy,[5] by use of twelve high-angle reflections scanned manually on all four circles with a small receiver collimator.

Intensity Measurements.—Intensity data were collected on a Hilger and Watts four-circle diffractometer by use of Mo-$K_{\bar{\alpha}}$ radiation utilising the method of balance filters, for a maximum 2θ angle of 50°. The θ, ω scan technique was used with a scan rate of 1° min^{-1} for a constant scan width of 1·4°. The background radiation was counted for 15 s at both extremes of the scan range with both the crystal and counter stationary. Reflections for which $I_o < 3\,\sigma\,(I_o)$ were rejected, the remainder being corrected for Lorentz polarisation factors. A total of 917 reflections was obtained. No correction for absorption (μR *ca.* 0·3), extinction, or anomalous dispersion of the cobalt atom was applied.

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods assuming the *Pnma* space group which was suggested by the vector distribution on the three-dimensional Patterson map. The carbon atoms of the ethylene bridge and those of the vinyl group clearly appeared disordered. In fact the electron-density maps show that the vinyl group lies out of the crystallographic mirror plane, and the ethylene bridge is located in two symmetrical arrangements, each carbon atom having an occupancy factor *F* of 0·5.

This suggests the possibility that, because of small distorsion from exact mirror symmetry of the molecule, the structure could belong to the non-centrosymmetric space group $Pna2_1$ (after interchanging of *b* and *c* axes). Therefore an isotropic full-matrix least-squares refinement has been carried out adopting both space-groups. After five cycles, acceptable values of bond lengths and angles were obtained only for the centrosymmetric space group. In fact the corresponding bond lengths of the two chemically equivalent halves of the molecule were quite different after the non-centrosymmetric refinement and often meaningless, *e.g.* in the pyridine molecule the N–C distances were 1·26 and 1·44 Å, whereas the C–C distances ranged from 1·19 to 1·56 Å. A further anisotropic refinement was then carried out in space group *Pnma*, with all atoms treated anisotropically except for the carbon atoms of the ethylene and vinyl groups. The contribution of the hydrogen atoms of the carbon atoms with occupancy factor 1·0 was then included and held constant ($B = 5{\cdot}0$ Å^2) in the last refinement which reduced *R* to 0·070. The minimised function was $\Sigma(w|F_o| - |F_o|)^2$. The expression used for the weighting factor was $w = (A + B|F_o| +$

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† bae = Dianion of bis(acetylacetone)ethylenedi-imine.

‡ salen = Dianion of bis(salicylaldehyde)ethylenedi-imine.

[1] G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc.* (*A*), 1970, 2870, and references therein.

[2] R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, **47**, 20.

[3] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601.

[4] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1971, 2720.

[5] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

$|C|F_o|^2)^{-1}$ where $A = 0{\cdot}11$, $B = 7{\cdot}94 \times 10^{-3}$, and $C = 1{\cdot}35 \times 10^{-4}$, were chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$. The final atomic parameters are listed in Table 1, together with their estimated standard deviations as derived from the residuals and the diagonal elements of the inverse matrix of the last cycle of the refinement. The numbering scheme for the atoms is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20373 (6 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates and thermal parameters * with their estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	F
Co	0·1701(1)	0·2500	0·0531(3)	2·07(5)	3·73(7)	1·88(6)	0	0·16(6)	0	0·5
O	0·1429(4)	0·3213(4)	−0·1412(9)	3·57(26)	4·05(29)	2·51(26)	0·77(22)	−0·41(22)	0·36(24)	1·0
N(1)	0·1989(5)	0·3207(5)	0·2437(11)	4·00(34)	5·05(40)	2·14(31)	1·49(31)	−0·77(28)	−0·78(31)	1·0
N(2)	0·2956(6)	0·2500	−0·0537(16)	2·44(35)	3·03(43)	2·74(43)	0	0·40(40)	0	0·5
C(1)	0·1355(5)	0·3941(5)	−0·1111(14)	2·82(35)	3·75(44)	4·40(50)	0·18(32)	−0·24(34)	0·12(39)	1·0
C(2)	0·1030(6)	0·4367(5)	−0·2683(16)	3·64(42)	3·71(45)	4·91(52)	−0·16(34)	0·12(41)	0·55(42)	1·0
C(3)	0·0906(7)	0·5126(6)	−0·2508(20)	5·55(60)	4·02(55)	6·67(67)	−0·44(43)	0·96(54)	0·36(56)	1·0
C(4)	0·1115(8)	0·5469(6)	−0·0730(23)	6·85(67)	3·88(48)	9·14(99)	−0·05(46)	0·20(72)	0·58(59)	1·0
C(5)	0·1459(7)	0·5085(6)	0·0784(20)	5·28(51)	4·67(52)	6·91(79)	−0·37(40)	0·43(53)	−1·79(56)	1·0
C(6)	0·1571(5)	0·4296(6)	0·0658(16)	3·36(38)	4·82(46)	4·48(53)	0·22(34)	0·35(40)	−1·87(46)	1·0
C(7)	0·1900(6)	0·3912(7)	0·2320(15)	3·37(45)	7·16(65)	3·55(46)	0·55(40)	0·14(35)	−1·01(48)	1·0
C(11)	0·3367(6)	0·3142(6)	−0·0905(14)	3·01(37)	4·40(4)	4·20(49)	−0·45(35)	−0·27(35)	0·36(34)	1·0
C(12)	0·4174(6)	0·3156(6)	−0·1620(16)	3·25(37)	5·03(48)	4·18(47)	−1·13(36)	−0·12(37)	1·25(44)	1·0
C(13)	0·4593(8)	0·2500	−0·1969(21)	2·64(52)	7·08(104)	3·49(75)	0	0·88(51)	0	0·5
				B/Å^2						
C(8,1)	0·2102(12)	0·2799(10)	0·4463(32)	4·17(38)						0·5
C(8,2)	0·2491(12)	0·2034(11)	0·4099(29)	4·29(42)						0·5
C(9)	0·0576(9)	0·2318(8)	0·1478(24)	2·95(37)						0·5
C(10)	0·0052(14)	0·2840(12)	0·2041(34)	5·08(91)						0·5
H(2)	0·0868	0·4086	−0·4079	5·0						
H(3)	0·0654	0·5455	−0·3746	5·0						
H(4)	0·0983	0·6067	−0·0560	5·0						
H(5)	0·1661	0·5386	0·2121	5·0						
H(7)	0·2098	0·4258	0·3578	5·0						
H(12)	0·4481	0·3686	−0·1920	5·0						

* Anisotropic temperature factors are defined by the expression: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Atomic scattering factors were calculated according to the expression $f(\mathrm{x}) = A \exp(-a\mathrm{x}^2) + B \exp(-b\mathrm{x}^2) + C$, where $\mathrm{x} = \sin\theta/\lambda$ and the constants were those given in ref. 6.

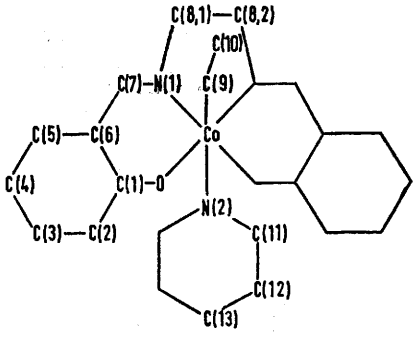

FIGURE 1 Numbering scheme for the atoms

Calculations.—All calculations were performed on an IBM 7044 computer, using programmes described in refs. 7 and 8. A programme of our own design (unpublished) was used to calculate best molecular planes. Least-squares plane equations were calculated according to ref. 9.

DISCUSSION

Description of the Structure.—The results of the X-ray analysis show that the crystal consists of discrete molecules with distorted octahedral stereochemistry around the cobalt atom. The salen ligand occupies the four equatorial positions, whereas the vinyl group and the pyridine molecule occupy the axial positions. The crystallographic mirror plane relates the two salicylaldimine residues of the equatorial ligand and half the pyridine molecule, the whole compound attaining the apparent m symmetry by statistical disorder of the vinyl group and ethylene bridge in the mirror plane. The equatorial donor atoms are exactly coplanar, the cobalt atom being slightly displaced (0·016 Å) towards the vinyl group. The crystallographic independent salicylaldimine residue is nearly planar (±0·04 Å), the angle between its plane and the equatorial co-ordination plane being 8·4°. Therefore the two halves of the equatorial ligand are bent towards the vinyl group at an angle of 16·8°. This umbrella-shape conformation is very similar to that found in the five-co-ordinated [Co(salen)(py)],[10] in which the angle between the two halves of the salen ligand was 28·8°. These values of the bending are

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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

[7] A. Immirzi, *Ricerca sci.*, 1967, **10**, 846.

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

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

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

easily interpreted in terms of different inter-ligand repulsion in the five- and six-co-ordinate species.

The plane passing through the pyridine molecule is nearly perpendicular to the equatorial plane (88·5°) and parallel to the N(1)–N(1′) direction as in the [Co(salen)(py)] compound.[10] Conversely the ethylene bridge is found in a nearly *gauche* conformation with a torsional angle around the C–C bond of 44·9°. It seems a general rule that for salen and bae cobalt complexes the ethylene bridge prefers a nearly *gauche* conformation in the octahedral species, whereas an eclipsed conformation is more easily assumed in the square planar and square pyramidal complexes. Table 2 lists a series of salen and bae cobalt derivatives together with the torsional angle around $H_2C–CH_2$ bond and the type of stereochemistry around the cobalt atom.

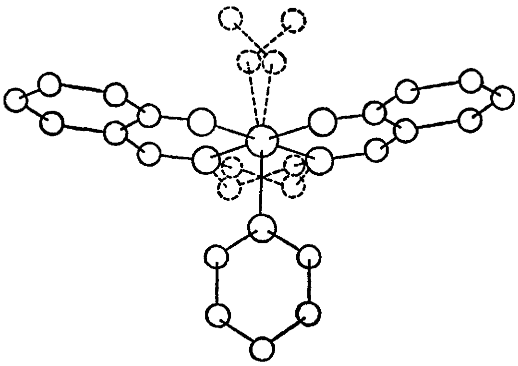

FIGURE 2 A side view of the molecule

The vinyl group is disordered in such a way that one half group is arranged above one salicyaldimine ring, the dihedral angle between the planes through Co, C(9), C(10) and N(1), Co, C(9) being 43·5°. The mirror symmetry relates the geometrical arrangement in the other half of the complex. A side view of the molecule is shown in Figure 2.

Bond lengths and angles are reported in Table 3 together with their estimated standard deviations.

The values of the interatomic bond distances in the salen ligand are in agreement, within experimental errors, with the mean values recently reported for a series of salen complexes.[11] The Co–C(sp^2) bond length is 1·93(2) Å. Correction from sp^2 to sp^3 carbon σ-covalent radius gives a value of 1·95 Å which must be compared with the average Co–C(sp^3) bond length found in other salen organometallic derivatives (2·00 Å). Because of the low accuracy of the carbon atom location this difference does not appear significant. However we note that the same difference is found in the corresponding bae organocobalt derivatives [Co–C(vinyl) 1·89 Å and Co–C(sp^3) 1·95 Å].[12]

TABLE 2

Conformation of the ethylene bridge and stereochemistry of some salen and bae cobalt complexes

	ϕ(°)	Stereochemistry
$[Co(salen)]_2$ [a]	38·7	Square-planar pyramid *
$[Co(salen)]\cdot CHCl_3$ [b]	10·8	Square-planar
[Co(salen)(py)] [c]	0	Square-planar pyramid
$[CH_3CH_2Co(salen)]_2$ [d]	44·0	Square-planar pyramid *
$[Co_2(salen)_2O_2(dmf)_2]$ [e]	39·5	Octahedral
$[(MeCO\cdot CH_2)Co(salen)(MeOH)]$	37·9	Octahedral
[(MeO)Co(salen)(py)] [f]	43·0	Octahedral
$[(CN\cdot CH_2)Co(salen)]_n$ [f]	34·6	Octahedral
$[(CH_2{:}CH)Co(salen)(py)]$ [g]	44·9	Octahedral
$[PhCo(bae)(H_2O)]$ [h]	32·9	Octahedral
[MeCo(bae)] [i]	2·2	Square-planar pyramid
$[(CH_2{:}CH)Co(bae)(H_2O)]$ [j]	42·6	Octahedral
$[Co(bae)],C_6H_6$ [k]	0	Square planar

* These compounds have a dimeric structure, where strong nonbonded interactions significantly alter the overall conformation.

[a] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, **B25**, 1969, 1671. [b] W. P. Schaefer and R. E. Marsh, *Acta Cryst.*, **B25**, 1969, 1675. [c] Ref. 10. [d] Ref. 4. [e] M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.* (*A*), 1970, 1069; dmf = dimethylformamide. [f] M. Cesari, C. Neri, G. Perego, E. Perrotti, and A. Zazzetta, *Chem. Comm.*, 1970, 276. [g] Present work. [h] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 152. [i] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1969, **3**, 308. [j] Ref. 12. [k] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1968, **2**, 386.

TABLE 3

Bond lengths (Å) and angles (°) with their estimated standard deviations in parentheses. Primed symbols refer to the corresponding atoms related by the crystallographic mirror plane

(*a*) Distances

Co–O	1·878(7)	C(1)–C(6)	1·39(1)
Co–N(1)	1·860(8)	C(2)–C(3)	1·38(1)
Co–N(2)	2·12(1)	C(3)–C(4)	1·39(2)
Co–C(9)	1·93(2)	C(4)–C(5)	1·35(2)
O–C(1)	1·32(1)	C(5)–C(6)	1·42(2)
N(1)–C(7)	1·27(2)	C(6)–C(7)	1·42(2)
N(1)–C(8,1)	1·56(2)	C(8,1)–C(8,2)	1·52(3)
N(1)–C(8,2′)	1·44(2)	C(9)–C(10)	1·31(3)
N(2)–C(11)	1·34(1)	C(11)–C(12)	1·37(1)
C(1)–C(2)	1·40(1)	C(12)–C(13)	1·37(1)

(*b*) Angles

O–Co–O′	85·4(3)	O–C(1)–C(2)	116·8(8)
O–Co–N(1′)	179·0(3)	O–C(1)–C(6)	131·9(9)
O–Co–N(1)	94·5(3)	C(2)–C(1)–C(6)	119·4(9)
O–Co–N(2)	88·8(3)	C(1)–C(2)–C(3)	121·5(10)
O–Co–C(9)	97·6(5)	C(2)–C(3)–C(4)	118·4(11)
O′–Co–C(9)	84·0(6)	C(3)–C(4)–C(5)	121·9(10)
N(1)–Co–N(1′)	84·4(5)	C(4)–C(5)–C(6)	120·7(11)
N(1)–Co–N(2)	90·2(3)	C(1)–C(6)–C(5)	118·1(10)
N(1)–Co–C(9)	96·6(5)	C(1)–C(6)–C(7)	123·3(10)
N(1′)–Co–C(9)	83·4(5)	C(5)–C(6)–C(7)	118·6(10)
Co–O–C(1)	125·5(6)	N(1)–C(7)–C(6)	124·9(10)
Co–N(1)–C(7)	127·1(7)	N(1)–C(8,1)–C(8,2)	109·0(15)
Co–N(1)–C(8,1)	108·5(8)	N(1′)–C(8,2)–C(8,1)	99·7(14)
Co–N(1)–C(8,2′)	118·1(10)	Co–C(9)–C(10)	124·6(13)
C(7)–N(1)–C(8,1)	122·1(10)	N(2)–C(11)–C(12)	122·4(10)
C(7)–N(1)–C(8,2)	114·0(11)	C(11)–C(12)–C(13)	120·0(10)
Co–N(2)–C(11)	121·4(6)	C(12)–C(13)–C(12′)	117·8(11)
C(11)–N(2)–C(11′)	117·3(9)		

trans- *and* cis-*Influence.*—The most important result arising from the comparison of the axial bond lengths in this and analogous compounds is the evidence of *trans*- and *cis*-influence in octahedral cobalt complexes.

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

[12] S. Brückner, M. Calligaris, G. Nardin, and L Randaccio, *Inorg. Chim. Acta*, 1968, **2**, 416.

TABLE 4

Correlation between Co–X bond lengths (Å) and Co–L $S^2/\Delta E$ values in salen octahedral cobalt complexes

Compound	L	X	Co–X	$S^2/\Delta E$* ($eV^{-1}.10^{-2}$)
$[ClCo(salen)]_2$ [a]	–Cl	–O	1·995(13)	<0·9
$[EtCo(salen)]_2$ [b]	$-CH_2CH_3$	–O	2·342(3)	1·4
$[(MeO)Co(salen)(py)]$ [f]	$-OCH_3$	–N	2·031(9)	<0·9
$[(CN{\cdot}CH_2)Co(salen)]_n$ [f]	$-CH_2CN$	–N	2·092(17)	1·4
$(CH_2{:}CH)Co(salen)(py)]$ [g]	$-CH{=}CH_2$	–N	2·119(10)	1·5
$[Co_2(salen)_2O_2(dmf)_2]$ [e]	$-O_2$	–O	2·150(7)	<0·9
$[(MeCO{\cdot}CH_2)Co(salen)(MeOH)]$ [f]	$-CH_2COCH_3$	–O	2·02(9)	1·4

* Data from Ref. 3.

[a] B. C. Wang and W. P. Schaefer, personal communication. [b] Ref. 4. [e–g] See footnotes to Table 2.

A simple model has been recenly suggested to explain the *trans*-influence in square planar [2] and octahedral complexes.[3] This is that in an X–M–L system the *trans*-influencing ability of the ligand L increases with increase of the ratio $S^2/\Delta E$, where S is the overlap integral between the L σ-hybrid and metal $p\sigma$ orbitals, and ΔE is their absolute energy separation. This hypothesis has found support for a series of Pt^{II} [2] square planar and d^6 octahedral complexes.[3]

TABLE 5

Co–C bond lengths (Å) in some organo-cobalt complexes

Compound	Co–C	Mean Co–C(sp^3)	*cis*-Ligand
$[(MeO_2C{\cdot}CH_2)Co(dmg)_2(py)]$ [a]	2·040(6)	2·04	dmg
$[EtCo(salen)]_2$ [b]	1·990(7)	2·00	salen
$[(NC{\cdot}CH_2)Co(salen)]_n$ [c]	2·02(1)		
$[(MeCO{\cdot}CH_2)Co(salen)(MeOH)]$ [c]	1·99(2)		
$[(CH_2{:}CH)Co(salen)(py)]$ [d]	1·93(2)		
$[MeCo(bae)]$ [e]	1·95(2)	1·95	bae
$[PhCo(bae)(H_2O)]$ [f]	1·93(2)		
$[(CH_2{:}CH)Co(bae)(H_2O)]$ [g]	1·89(1)		

[a] P. C. Lenhert, *Chem. Comm.*, 1967, 980. [b] Ref. 4. [c] Ref. *f* of Table 2. [d] Present work. [e–g] Refs. *i*—*k* of Table 2.

We have applied the same model to interpret the *trans*-influence in the salen octahedral complexes as shown from the data of Table 4. It can be seen that in all three cases reported, the Co–X distance increases with the increasing of the $S^2/\Delta E$ ratio; however the agreement between the two trends is only qualitative.

The Co–C bond lengths in this and similar complexes are listed in Table 5.

The values seem to be indicative of a *cis*-influence of the different quadridentate equatorial ligands salen, bae, and dimethylglyoximate (dmg) on the Co–C axial bond lengths, which increase in the order bae < salen < dmg. The same trend has been already observed for other properties of these complexes.[13]

We are grateful to Professor R. Mason for allowing us to use the Hilger and Watts diffractometer of the Department of Chemistry in the University of Sheffield, and B. Law for help in collecting data. This research has been in part supported by C.N.R., Rome (Italy).

[1/1223 *Received*, 19*th July*, 1971]

[13] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta, Rev.*, 1970, **4**, 1971.