Structural Effects of the Co-ordination of Quadridentate Schiff Bases to Transition-metal Atoms. Structure of *NN'*-(*o*-phenylene)bis(salicylideneamine) and of its Cobalt(II) Complex

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Geometrical variations which occur when a quadridentate Schiff-base co-ordinates to a cobalt(II) atom are compared on the basis of the crystal structure analysis of the ligand *NN'*-(*o*-phenylene)bis(salicylideneamine) (I) and its Co^{II} derivative in its orthorhombic (II) and monoclinic (III) modifications. Crystals of (I) are monoclinic, space group $P2_1/c$, with cell parameters: a = 6.064(3), b = 16.541(7), c = 13.306(7) Å, β = 91.5(1)°. Crystals of (II) are orthorhombic, space group $P2_12_12_1$ with a = 16.755(7), b = 17.532(8), c = 5.362(3) Å, and of (III) are monoclinic, space group $P2_1/n$, with a = 10.681(5), b = 8.354(4), c = 18.185(8) Å, β = 105.3(1)°. A total of 1 277 (I), 1 113 (II), and 2 558 (III) independent reflexions were used; the structures were solved from diffractometer data by the heavy-atom method and refined to final R factors of 0.056 (I), 0.046 (II), and 0.041 (III). The enolimine form is established for (I) in the solid state. Upon co-ordination, with formation of (II) and (III), the geometrical data suggest that the contribution to the resonance of a ketamine form becomes as important as that of the enolimine. This is in agreement with a π-orbital delocalization of the electronic charge over the planar complex molecule.

QUADRIDENTATE Schiff-base cobalt complexes have been intensively studied. Their ability to form stable organometallic derivatives,[1,2] to bind reversibly molecular oxygen[3-5] and carbon dioxide[6] to the metal centre, and to act as complex ligand[7] for alkali-metal ions and other metallic elements[8] has been widely investigated and discussed in terms of electronic and structural properties.

Although recently some studies have been reported for the free ligands,[9] there is no information available on

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[8] M. Calligaris, L. Randaccio, R. Barbieri, and L. Pellerito, *J. Organometallic Chem.*, 1974, **76**, C56.

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their structural features as well as on the geometrical variations which occur in the ligand when it is co-ordinated to the metal atom. Because electronic variations may have structural implications, a geometrical study of the free and co-ordinated ligand may be useful to obtain further insight into the bonding between cobalt and macrocycle ligands. We have therefore undertaken the crystal structure determination of a series of free quadridentate ligands and their cobalt(II) derivatives. We report here the crystal structure of the neutral ligand *NN'*-(*o*-phenylene)bis(salicylideneamine) [salph-H_2; (I)] and of its Co^{II} derivative, [Co(salph)]. The [Co(salph)] shows polymorphism, crystallising in two different modifications, one orthorhombic (II) the other monoclinic (III).

EXPERIMENTAL

Crystal Data.—(*a*) $C_{20}H_{16}N_2O_2$, (I), $M = 316.0$, Monoclinic, $a = 6.064(3)$, $b = 16.541(7)$, $c = 16.306(7)$ Å, $\beta = 91.5(1)°$, $U = 1\,635.0$ Å^3, $D_m = 1.26(1)$, $Z = 4$, $D_c = 1.28$. Space group $P2_1/c$. (*b*) $C_{20}H_{14}CoN_2O_2$, (II), $M = 373.0$, Orthorhombic, $a = 16.755(7)$, $b = 17.532(8)$, $c = 5.362(3)$ Å, $U = 1\,575.1$ Å^3, $D_m = 1.59(1)$, $Z = 4$, $D_c = 1.574$. $\mu = 11.5$ cm^{-1}, $\mu.r = 0.12$. Space group $P2_12_12_1$; (*c*) $C_{20}H_{14}CoN_2O_2$, (III), Monoclinic, $a = 10.681(5)$, $b = 8.354(4)$, $c = 18.185(8)$ Å, $\beta = 105.3(1)°$, $U = 1\,564.9$ Å^3, $D_m = 1.62(1)$, $Z = 4$, $D_c = 1.58$, $\mu = 11.6$ cm^{-1}, $\mu.r = 0.28$. Space group $P2_1/n$.

TABLE 1

Positional parameters for salphH_2 (I), with estimated standard deviations in parentheses

	x	*y*	*z*
O(1)	−2 048(5)	6 480(2)	2 759(2)
O(2)	−3 411(5)	6 162(2)	4 821(2)
N(1)	1 043(6)	7 066(2)	3 749(2)
N(2)	−1 111(6)	7 433(2)	5 143(2)
C(1)	−608(7)	5 886(3)	2 594(3)
C(2)	−1 257(9)	5 276(3)	2 041(3)
C(3)	207(9)	4 659(3)	1 874(3)
C(4)	2 302(9)	4 618(3)	2 261(3)
C(5)	2 967(8)	5 217(3)	2 804(3)
C(6)	1 537(8)	5 862(3)	2 971(3)
C(7)	2 312(8)	6 482(3)	3 529(3)
C(8)	1 923(8)	7 686(3)	4 258(3)
C(9)	3 878(8)	8 106(3)	4 043(3)
C(10)	4 634(8)	8 752(3)	4 522(3)
C(11)	3 427(9)	8 988(3)	5 186(3)
C(12)	1 515(9)	8 571(3)	5 404(3)
C(13)	746(8)	7 922(3)	4 952(3)
C(14)	−2 300(8)	7 561(3)	5 770(3)
C(15)	−4 176(8)	7 044(3)	5 941(3)
C(16)	−5 572(9)	7 215(3)	6 594(3)
C(17)	−7 428(9)	6 747(4)	6 750(3)
C(18)	−7 909(9)	6 090(3)	6 258(3)
C(19)	−6 561(9)	5 898(3)	5 614(3)
C(20)	−4 693(8)	6 360(3)	5 451(3)
H(1)	−1 400	6 850	3 250
H(2)	−2 875	5 280	1 767
H(3)	−272	4 206	1 446
H(4)	3 362	4 108	2 154
H(5)	4 582	5 212	3 076
H(7)	3 969	6 450	3 773
H(9)	4 753	7 927	3 518
H(10)	6 112	9 060	4 364
H(11)	3 993	9 499	5 542
H(12)	651	8 747	5 955
H(14)	−1 872	7 985	6 247
H(16)	−5 225	7 726	6 981
H(17)	−8 446	6 893	7 254
H(18)	−9 356	5 738	6 358
H(19)	−6 918	5 381	5 243
H(20)	−2 100	6 550	4 800

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with a Siemens diffractometer using Mo-K_α radiation ($\lambda = 0.710\,7$ Å).

TABLE 2

Positional parameters for (II) with estimated standard deviations in parentheses

	x	*y*	*z*
Co	2 800(1)	1 927(1)	6 493(2)
O(1)	3 770(3)	1 438(3)	6 385(12)
O(2)	3 203(3)	2 432(3)	9 253(11)
N(1)	2 394(3)	1 411(3)	3 704(12)
N(2)	1 826(4)	2 451(3)	6 523(14)
C(1)	4 029(5)	959(4)	4 754(16)
C(2)	4 826(5)	671(5)	5 015(19)
C(3)	5 137(5)	171(5)	3 334(19)
C(4)	4 686(5)	−104(5)	1 222(17)
C(5)	3 917(5)	169(5)	971(18)
C(6)	3 574(5)	683(5)	2 704(15)
C(7)	2 794(5)	931(4)	2 248(14)
C(8)	1 597(4)	1 629(4)	3 116(15)
C(9)	1 137(5)	1 320(5)	1 126(17)
C(10)	364(5)	1 610(5)	764(18)
C(11)	52(5)	2 154(5)	2 333(20)
C(12)	500(5)	2 442(5)	4 353(18)
C(13)	1 291(4)	2 175(4)	4 657(16)
C(14)	1 640(4)	3 042(5)	7 970(14)
C(15)	2 126(5)	3 322(4)	9 920(15)
C(16)	1 836(6)	3 956(4)	11 309(19)
C(17)	2 290(5)	4 258(5)	13 278(17)
C(18)	3 024(6)	3 915(5)	13 883(17)
C(19)	3 332(5)	3 322(5)	12 554(17)
C(20)	2 889(4)	3 006(5)	10 479(15)
H(2)	4 950	−460	−150
H(3)	5 720	−60	3 660
H(4)	5 140	880	6 490
H(5)	3 610	−40	−560
H(6)	2 450	760	600
H(7)	8	1 360	−700
H(8)	1 390	963	−180
H(9)	−590	2 340	2 000
H(10)	270	2 870	5 590
H(11)	1 040	3 210	7 720
H(12)	3 925	3 110	12 940
H(13)	3 320	4 170	15 370
H(14)	2 015	4 710	14 320
H(15)	1 260	4 190	10 890

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by means of the θ—2θ scan technique and Mo-K_α radiation for $2\theta_{max.}$ 54° for all three compounds. Reflexions having $I_o < 3\sigma(I_o)$ were rejected, the remainder being corrected for Lorentz and polarization factors. A total of 1 277 (I), 1 113 (II), and 2 558 (III) independent reflexions were used in the subsequent calculations. No correction for absorption and anomalous dispersion of cobalt was applied.

Structure Determination and Refinement.—The structure of (I) was solved by direct methods using the Multan program.[10] The *E* map based on the phases obtained for the 170 reflexions with $|E| > 1.4$ revealed all 24 crystallographically independent non-hydrogen atom positions. After anisotropic block-diagonal matrix least-squares

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[10] G. Germain, P. Main, and M. N. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

refinement, a difference-Fourier synthesis was calculated, in which the estimated positions of hydrogen atoms were all in regions of positive electron density. The final anisotropic refinement, including the contribution of the hydrogen atoms held constant (B 5.0 Å^2), gave R 0.056. The structures of (II) and (III) were solved by the conventional heavy-atom method. Final anisotropic refinement, including the contribution of hydrogen atoms held constant at calculated positions, gave R 0.046 (II) and 0.041 (III). Final weighting schemes were $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 4.75$, $B = 1.0$, $C = 0.008$ for (I), $A = 8.6$, $B = 1.0$, $C = 0.007$ for (II), and $A = 3.9$, $B = 1.0$, $c = 0.05$ for (III), the values of the constants being chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin \theta/\lambda)$.

TABLE 3

Positional and thermal parameters for (III) with estimated standard deviations in parentheses

	x	y	z
Co	502(0)	3 419(1)	4 667(0)
O(1)	−1 049(2)	2 358(3)	4 297(1)
O(2)	222(3)	4 138(4)	3 681(1)
N(1)	791(3)	2 613(4)	5 657(2)
N(2)	2 076(3)	4 511(4)	5 027(2)
C(1)	−1 630(3)	1 404(5)	4 659(2)
C(2)	−2 861(4)	788(6)	4 263(2)
C(3)	−3 520(4)	−280(6)	4 608(3)
C(4)	−3 004(4)	−754(6)	5 367(3)
C(5)	−1 825(4)	−156(6)	5 763(2)
C(6)	−1 116(4)	942(5)	5 433(2)
C(7)	77(4)	1 566(5)	5 887(2)
C(8)	1 963(4)	3 207(5)	6 167(2)
C(9)	2 414(4)	2 819(6)	6 932(2)
C(10)	3 587(4)	3 497(6)	7 356(2)
C(11)	4 264(4)	4 533(6)	7 013(2)
C(12)	3 814(4)	4 939(6)	6 248(2)
C(13)	2 656(3)	4 240(5)	5 822(2)
C(14)	2 649(4)	5 399(5)	4 620(2)
C(15)	2 150(4)	5 734(5)	3 834(2)
C(16)	2 842(4)	6 780(6)	3 465(3)
C(17)	2 373(5)	7 191(7)	2 715(3)
C(18)	1 175(5)	6571(6)	2 298(2)
C(19)	486(4)	5 557(6)	2 625(2)
C(20)	939(4)	5 100(5)	3 400(2)
H(2)	−3 280	1 160	3 690
H(3)	−4 440	−730	4 290
H(4)	−3 510	−1 570	5 630
H(5)	−1 420	−520	6 340
H(7)	400	1 140	6 450
H(9)	1 880	2 020	7 190
H(10)	3 930	3 210	7 940
H(11)	5 160	5 020	7 330
H(12)	4 340	5 760	5 980
H(14)	3 560	5 910	4 900
H(16)	3 750	7 240	3 780
H(17)	2 900	7 970	2 440
H(18)	810	6 900	1 710
H(19)	−420	5 090	2 280

Final atomic parameters are listed in Tables 1—3, 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 schemes for the atoms are shown in Figure 1(a) for (I) and Figure 1(b) for (II) and (III). Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21 816 (18 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 11.

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described previously.[5]

RESULTS

Structure of (I).—A view of the salphH_2 molecule is shown in Figure 2(a). The molecules are held together in the crystal only by van der Waals forces.

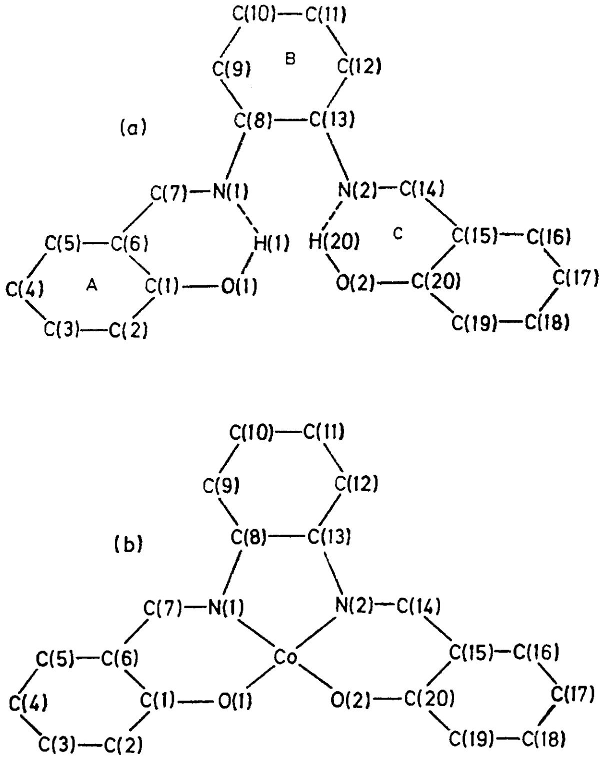

FIGURE 1 Numbering scheme for the atoms of (a) salphH_2 and (b) the two crystalline forms of [Co(salph)]

Intramolecular hydrogen bonds occur between the pairs of atoms O(1), N(1) [2.628(6) Å] and O(2), N(2) [2.570(6) Å], the hydrogen atoms, located on the difference Fourier map, being essentially bound to the oxygen atoms. The O(1)–H(1) and O(2)–H(20) distances are 1.07 and 1.02 Å and the O(1)–H(1)–N(1) and O(2)–H(20)–N(2) angles are 140 and 144°, respectively. This result and other conclusions (*vide infra*) suggest the enolimine tautomeric structure (Ia) is preferred to the ketamine one (Ib) (Scheme 1) in the solid state. The endolimine form has also been suggested[9] for *NN'*-ethylenebis(salicylideneamine) (salenH_2) and some of its derivatives. However inter- and intra-molecular hydrogen bonds have been detected in solution. On the other hand, the ketamine structure has been suggested[12] for the Schiff base *NN'*-ethylenebis(pentane-2,4-diamine) (acacen-H_2). Furthermore Gullotti *et al.*[9] have recently suggested for acacenH_2 and some of its ethylene-bridge substituted derivatives that hydrogen bonds occur between the oxygen atoms of one moiety of the molecule and the nitrogen atoms of the other, giving a ketamine ' flyover ' structure.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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

[12] G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 2099.

In our case, the hydrogen bond formation in the same salicylideneamine residue prevents planarity of the whole molecule, as shown in Figure 2(a), its geometry being determined by a rotation around the N(1)–C(8) bond of 52°. Thus the corresponding salicylideneamine residue is removed from the plane of all the other atoms of the molecule, the mean planes of the two salicylideneamine residues making an angle of 56.8°.

Figure 2(b) shows distances and angles of interest. Analysis of phenyl bond lengths and angles is in agreement with the 'delocalized' rings shown in Scheme 1, means for each of the three rings being **1.401(7) Å** and **119.7(5)°** for A, **1.398(7)** Å and 120.0(5)° for B, and **1.396(7)** Å and 120.0(5)° for C (see Figure 1). Taking into account that other resonance structures can 'superimpose' to the simple formula (Ia), however, all other bond lengths strongly suggest this form to be predominant, confirming the tautomeric enolimine structure. The mean N=CH and O–C bond lengths are **1.288(6)** and **1.345(6)** Å. The latter value is not far from values recently reported for salicylates and phenol derivatives[13] [1.355(2) — 1.377(4) Å]. The former is in the range of values reported for double N=C bond[14] [1.262(4)—1.281(9) Å]. However, the N(1)–C(8) distance [1.415(6) Å] must be assumed to be essentially a single N(sp^2)–C(sp^2) bond since the torsion angle (52°) around it allows little π-bonding overlap. Another consequence of the different conformation of the two moieties of the molecule is reflected in the N(1)–C(8)–C(9) and N(2)–C(13)–C(12) angles [120.8(4) and 125.7(4)°]. The increase of *ca.* 5° in the latter alleviates steric interaction between atoms H(12) and H(14), which in the planar conformation is larger than that between the corresponding atoms H(7) and H(9), which are moved apart (2.53 Å) by the torsion around the N(1)–C(8) bond. This is confirmed (*vide infra*) by the means of these angles [124.3(7) in (II) and 125.3(4)° in (I)] in the [Co(salph)] molecules, which are, as a whole, quite planar. Other bond angles are as expected, and similar in the two salicylideneamine residues.

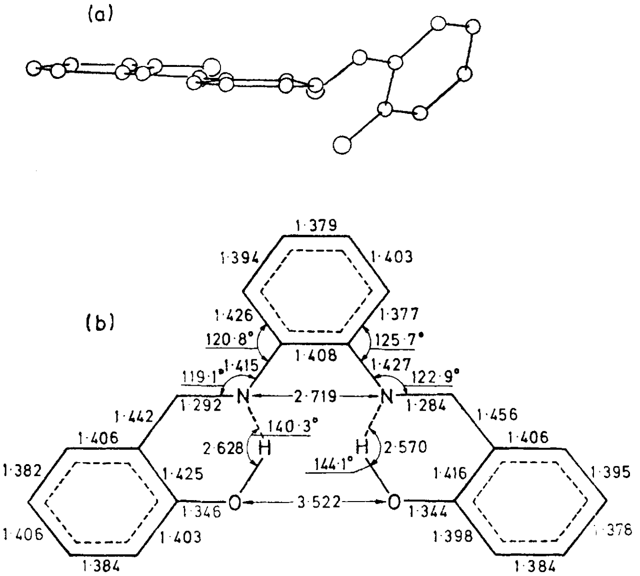
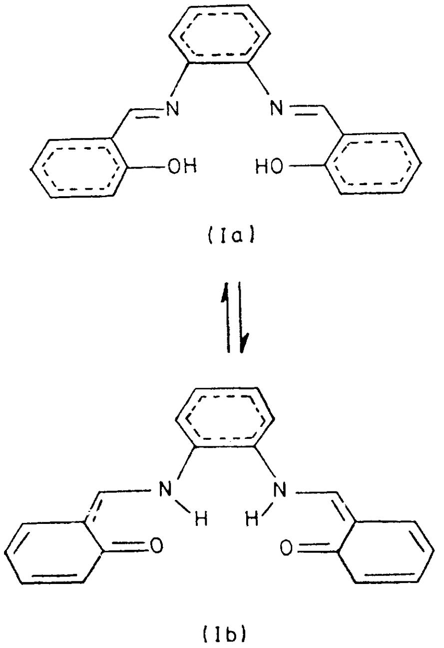


FIGURE 2 (a) A view of the salphH$_2$ molecule, and (b) bond lengths (Å) and angles (°) of interest; mean estimated standard deviations: C–C 0.007, C–N(O) 0.006 Å; angles 0.5°



(Ia)

(Ib)

Structure of [Co(salph)].—Although it crystallizes in two modifications, the [Co(salph)] molecules in the two cases differ only in their planarity (Figure 3), where side views of the molecules in the two types of crystals are compared. The orthorhombic structure (II) exhibits molecules slightly distorted towards an umbrella-shape, in contrast with the more planar molecules of the monoclinic form (III). This is probably due to the different crystal packing. The cobalt atom in both structures has an approximately planar geometry with deviations of the metal and its donor atoms from their mean plane not exceeding ±0.03 Å.

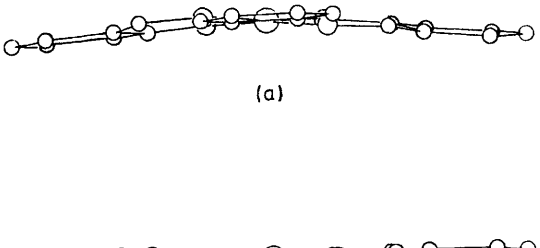


FIGURE 3 Side views of (II) (a) and (III) (b). Deviations (Å) of atoms from the co-ordination plane: (II) N 0.015, N −0.021, O −0.021, O 0.015, Co 0.012); (III) N −0.018, N 0.012, O 0.012, O −0.018, Co 0.012

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[13] D. Tsoucaris, G. de Rango, G. Tsoucaris, C. H. Zelwer, R. Parthasarathy, and F. E. Cole, *Cryst. Struct. Comm.*, 1973, **2**, 193; J. P. Beale, *ibid.*, p. 125; M. Cotrait and J. P. Bideau, *ibid.*, p. 111; K. Venkatasubramanian, *ibid.*, 1972, **1**, 427.

[14] F. Plana, C. Miravitlles, J. L. Briansó, and M. Foltalbana, *Cryst. Struct. Comm.*, 1974, **3**, 135; A. M. Manotti Lanfredi and A. Tiripicchio Camellini, *ibid.*, 1975, **4**, 141.

Table 4

Comparison of co-ordination and C–O and CH–N bond lengths (Å) in some quadridentate Schiff-base cobalt(II) derivatives

	Co–O	Co–N	C–N [a]	C–O [b]
Four-co-ordinate				
[Co{salbn(+)}] [b,c]	1.845(7) 1.851(7)	1.880(9) 1.852(9)	1.28(1)	1.31(1)
[Co{salbn(m)}] [b,c]	1.848(3) 1.861(2)	1.878(3) 1.860(3)	1.304(5)	1.319(6)
[Co{salchx(m)}] [d,e]	1.855(10) 1.853(10)	1.879(11) 1.878(12)	1.309(17)	1.316(15)
[Co(salen)] [f]	1.835(4) 1.869(5)	1.864(5) 1.829(5)	1.284(9)	1.305(7)
[Co(salph)] [g]	1.842(2) 1.839(2)	1.870(4) 1.872(3)	1.305(6)	1.298(5)
[Co(salph)] [h]	1.838(5) 1.852(6)	1.876(6) 1.873(7)	1.330(10)	1.300(10)
Five-co-ordinate				
[{Co(salen)}$_2$] [i]	1.901(4) 1.940(4)	1.886(5) 1.907(5)	1.295(8)	1.318(7)
[Co(salen)]·py [j]	1.90(1)	1.90(1)	1.27(2)	1.36(2)
[Co{salbn(+)}]·py [k,c]	1.907(8) 1.904(7)	1.887(9) 1.851(9)	1.31(2)	1.30(1)

[a] Means of chemically equivalent bond lengths [b] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1973, 419. [c] salbn(+) and salbn(m) are the dianions of the optically active- and *meso*-forms of *NN'*-butylenebis(salicylideneamine). [d] Ref. 5. [e] salchx (+) is the dianion of *meso*-form of *NN'*-cyclohexylenebis(salicylideneamine). [f] W. P. Schaeffer and R.E. Marsh, *Acta Cryst.*, 1969, **B25**, 1675. [g] Present work, (III). [h] Present work, (II). [i] R. de Iasi, B. Post, and S. L. Holt, *Inorg. Chem.*, 1971, **10**, 1498. [j] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411. [k] N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 498.

Comparable bond lengths and angles (Figure 4) are similar in the two cases. The mean Co–N and Co–O distances [1.873(4) and 1.843(4) Å] are compared in Table 4 with corresponding bond lengths in other Co^{II} quadridentate Schiff-base derivatives. Table 4 shows that the Co–O are slightly, but significantly, shorter than Co–N distances, regardless of the type of the quadridentate ligand. Furthermore, no significant difference is detectable between [Co(salph)] and [Co(salen)]-type derivatives, although recently it has been suggested,[15] on the basis of ESCA results, that the metal–ligand interaction is more 'electrovalent' in [Co(salen)] than in [Co(salph)].

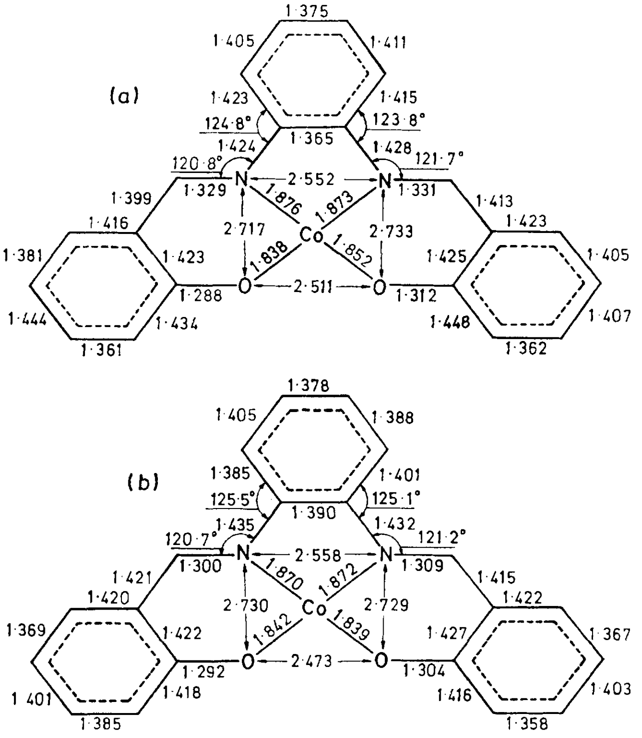

Figure 4 Bond lengths (Å) and angles (°) of interest for (II) (a) and (III) (b): mean estimated standard deviations: C–C 0.012 (II) and 0.006 Å (III); C–N(O) 0.009 (II) and 0.006 Å (III); Co–N(O) 0.006 (II) and 0.003 Å (III); angles involving cobalt and donor atoms 0.2 (II) and 0.1 (III), other angles 0.7 (II) and 0.4° (III)

Comparison of N–CH and C–O bond lengths shows that there are no significant variations for the compounds listed in Table 4.

DISCUSSION

To our knowledge the only accurate structural analysis of a ligand before[16] and after[17] co-ordination was carried out for glyoxime.

Although glyoxime (gmH$_2$) acts as a bidentate monoanion, it gives bisglyoximates of transition metals, such as Ni^{II} [17] [Ni(gmH)$_2$] in such a way that two bidentate molecules simulate a quadridentate ligand. The structural parameters of gmH$_2$ and [Ni(gmH)$_2$] molecules are reported in Figure 5(a). The ligand gmH$_2$ must change its *anti-s-trans*-conformation and the N–C–C angles in order to act as chelate ligand. Furthermore, the N–O distance and O–N–C angle increase by *ca.* 0.05 Å and *ca.* 10° respectively upon co-ordination, whereas the C–C and N–C distances do not change significantly, as already observed.[18] The variation of the O–N–C angle may be attributed to the formation of the strong O · · · O hydrogen bond, whereas the shortening of the N–O distance in [Ni(mgH)$_2$] has been attributed[17] to the 'partially ionized oxygen atoms which cause a mesomeric effect on N–O bonds.'

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[15] J. H. Burness, J. G. Dillard, and L. T. Taylor, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 825.

[16] M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, 1966, **20**, 73.

[17] M. Calleri, G. Ferraris, and D. Viterbo, *Acta Cryst.*, 1967, **22**, 468.

[18] A. Chakravorty, *Co-ordination Chem. Rev.*, 1974, **13**, 1.

This comparison suggests that π-delocalization in the plane of $[Ni(mgH)_2]$ complex is scarce. However, the following comparison between $salphH_2$ and [Co(salph)] indicates that the cobalt-atom electrons are much more involved in π-delocalized orbitals over the Schiff-base plane.

Besides the obvious variation of the ligand conformation and the bond angles of N–CH–C–C–O cycles to accommodate the metal atom, Figure 5(b) compares bond lengths averaged over two chemically equivalent halves of the free and co-ordinated ligand. The structural parameters of (III) are taken since they are more accurate than those of (II). Distances such as C(1)–O(1) and C(6)–C(7) (see numbering scheme) of $salphH_2$ are shortened by *ca.* 0.05 and 0.03 Å respectively in [Co(salph)], whereas other bond lengths are unchanged within 3σ. These two distances may be assumed to be essentially single in the enoliminic form established for $salphH_2$, *i.e.*, in Scheme 2 the resonance structures (a) and (b) are predominant with respect to structure (c). When co-ordination to cobalt takes place, the shortening of the C–O and C–C distances indicates that the contribution to the resonance of structure (c) becomes more important than in the free ligand. The other C–C bond lengths, which are already intermediate between a single and a double bond, are less affected. The slight lengthening, if significant, of the N–C bonds is consistent with this view. We note that in the less-accurately determined orthorhombic structure this lengthening is more enhanced. If such an interpretation is correct, the significant contribution of form (c) to the resonance of [Co(salph)] means that the electronic charge is spread over all the whole planar molecule, mainly through π-orbitals, including those of the metal centre, as already suggested [2] on the basis of the values of Co–N(O) distances.

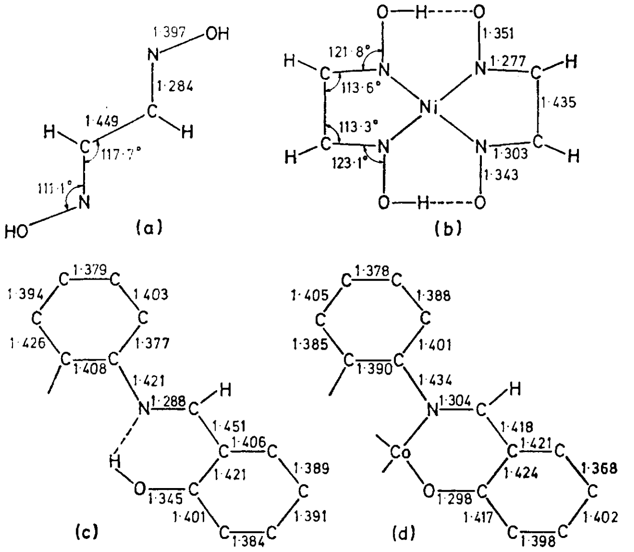
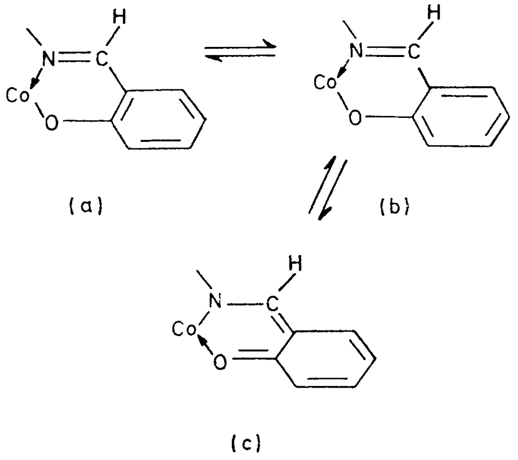
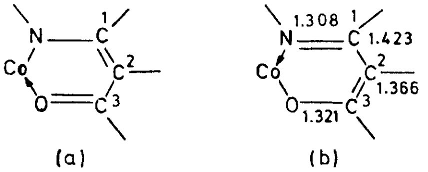


FIGURE 5 Comparison of geometries before and after co-ordination of gmH_2 and $salphH_2$: (a) gmH_2, (b) $[Ni(gmH)_2]$, (c) $salphH_2$, and (d) [Co(salph)]



An analogous conclusion may also be reached for [Co(acacen)]. Assuming that the free ligand has a ketamine structure,[9] the resonance form (a) of Scheme **3** must be predominant. In the [Co(acacen)] derivatives,[2] however, the C(1)–C(2) and C(2)–C(3) distances are 1.423 and 1.366 Å, in agreement with a considerable contribution from form (b). This result may be interpreted similarly to that discussed.



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