

Complexation with PdCl₂ causes ppfa to assume a conformation different from that observed in the crystal structures of the free ligand and the Rh(nbd) complex. There is a rotation of -65° about P-C(10) [-40° in (III)] and of -10° about C(9)-C(11) [-100° in (III)], compared with the free ligand. The rotation about P-C(10) brings one phenyl ring into proximity with the ferrocenyl moiety and forces this ring to be 'edge-on' to the Pd atom and the other ring to be 'face-on' [angles between the least-squares planes of the rings and of the coordination plane are 71 (1) and 88.0 (9)° respectively]. The distortion from tetrahedral geometry of C(11) is less than in (III) (probably due to the smaller metal-N and -P distance in the PdCl₂ complex), which causes less strain in the formation of the six-membered chelating ring. Puckering parameters [$Q = 0.63$ (2) Å, $\theta = 105$ (2)° and $\phi = 64$ (2)° for the sequence Pd-P-C(10)-C(9)-C(11)-N] indicate that the metalla-ring has a distorted boat conformation.

Bond lengths and angles are generally as expected. The Fe atom is located near the line between the centroids [Cp(*i*)] of the cyclopentadienyl rings [angle Cp(1)-Fe-Cp(2) = 176.6 (2)°] and lies 1.67 (8) Å beneath the plane of the unsubstituted ring and 1.64 (6) Å above the plane of the substituted ring, as is commonly observed in ferrocenyl derivatives.

In the crystal packing, the two disordered CDCl₃ molecules only fill the space between the (ppfa)PdCl₂

molecules and have weak interactions [shortest intermolecular contacts: Cl(2)···D(1) = 2.45 (2) and Cl(1)···D(2)(*x*,*y*,*z*-1) = 2.74 (2) Å].

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Structure of [*N,N'*-4-Methyl-4-azaheptane-1,7-diylbis(salicylideneiminato)]copper(II) Benzene Solvate

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Abstract. [Cu(C₂₁H₂₅N₃O₂)]₂·C₆H₆, *M_r* = 493.1, monoclinic, *P*2₁/*a*, *a* = 13.095 (3), *b* = 16.671 (4), *c* = 11.532 (3) Å, $\beta = 93.78$ (4)°, *V* = 2512 (1) Å³, *Z* = 4, *D_x* = 1.30 Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 8.95$ mm⁻¹, *F*(000) = 1036, *T* = 298 K, *R* = 0.073 for 1746 unique observed reflections. The structure is similar to that of the analogous Co^{II} compound. Crystals of both compounds are monoclinic and can be obtained from benzene solutions. The Cu atom is linked to three N and to two O atoms of the ligand and the coordination geometry is distorted trigonal bipyramidal. The O(1)-Cu-O(2) angle is 145.6 (3)°, 15.8° larger than the corresponding angle in the Co complex. The Cu-N(3) distance [2.337 (9) Å] is longer

than the Co-N(3) length [2.15 (1) Å]. Conversely, the other two Cu-N bond lengths [average 1.954 (8) Å] are shorter than the corresponding Co-N distances [average 2.04 (1) Å]. Again a disorder of the ligand's atoms bound to N(3) is present. The benzene molecule is almost coplanar with the equatorial coordination plane and lies in the proximity of the metal atom. An H atom belonging to the benzene molecule points towards the metal at a distance of 2.90 Å from the cation.

Introduction. Continuing structural investigations of *N,N'*-4-methyl-4-azaheptane-1,7-diylbis(salicylideneiminato) (hereafter SALMeDPT)-metal complexes and their dioxygen adduct to understand the stereo-

chemical requisites of the precursor, our recent attention was focused on the capability to add dioxygen shown also in the solid phase by a crystalline form (γ) of the SALMeDPT–Co^{II} complex containing cocrystallized benzene molecules (Cini & Orioli, 1983; Zanello, Cini, Cinquantini & Orioli, 1983). The benzene ring proved to be very close to the metal centre and almost coplanar with the equatorial O(1), O(2), N(3) plane. These data suggested that a sort of activation of the metal centre by the solvent occurs. In fact, for two different forms (α and β) of the SALMeDPT–Co^{II} complex, which either have no benzene at all or the solvent molecule is far from the metal cation, no reactivity towards dioxygen was observed at $T = 298$ K and $P_{O_2} = 0.1$ MPa in the solid state (Cini & Orioli, 1982).

With the aim to obtain a deeper insight into the geometrical features of SALMeDPT–metal complexes containing benzene molecules, the preparation of single crystals suitable for the X-ray diffraction technique was undertaken for compounds containing divalent 3d metal ions. Here we wish to report the structural parameters relevant to the Cu^{II} species.

Experimental. SALMeDPT–Cu^{II} (200 mg) obtained as reported by Sacconi & Bertini (1966) was dissolved in hot benzene (10 ml). On cooling, well shaped dark-green prisms separated. The compound was characterized by elemental analysis, and by infrared-spectroscopy measurements.

The crystals undergo some efflorescence at room temperature probably due to a superficial loss of benzene. For this reason the crystals were stored below 273 K.

Crystal $0.20 \times 0.10 \times 0.10$ mm, sealed in a glass capillary; Philips PW 1100 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters by least-squares refinement of 25 reflections ($20 \leq 2\theta \leq 25^\circ$); intensity data ($-12 \leq h \leq 12$, $0 \leq k \leq 16$, $0 \leq l \leq 11$) recorded in θ - 2θ scan mode for $4 \leq 2\theta \leq 40^\circ$, scan speed $0.05^\circ \text{ s}^{-1}$, scan width 1.6° background counted every 10 s; three standard reflections (630, $\bar{6}30$, $6\bar{3}0$) measured every 120 min showed a maximum 10% variation; 2166 reflections measured and empirically corrected for intensity decay; Lp corrections, ψ scans with minor variations of intensities, no absorption correction, 1746 unique reflections with $F_o \geq 3\sigma(F)$.

Heavy-atom method, anisotropic full-matrix least-squares refinement on F for all non-H atoms of ligand except C atoms linked to N(3) and benzene atoms; three new peaks found at bond distances from N(3) and nine H atoms from difference Fourier synthesis; benzene C atoms isotropic; nine H atoms isotropic with fixed temperature factor $U 0.08 \text{ \AA}^2$. Two sets of positions for the atoms C(17), C(20) and C(21) around N(3) were found. They were interpreted as a statistical disorder in

Table 1. Fractional coordinates ($\times 10^4$) and equivalent values U_{eq} of the anisotropic temperature factors U_{ij} or values of the isotropic temperature factors U ($\text{\AA}^2 \times 10^4$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}/U	Occupancy
Cu	3879 (1)	6266 (1)	2430 (1)	512 (9)	
O(1)	3864 (5)	6497 (4)	4086 (6)	657 (56)	1
O(2)	3776 (5)	6715 (4)	873 (6)	655 (53)	1
N(1)	2403 (6)	6089 (5)	2308 (8)	584 (60)	1
N(2)	5374 (6)	6338 (5)	2513 (7)	559 (56)	1
N(3)	4062 (8)	4874 (5)	2333 (7)	723 (80)	1
C(1)	2060 (7)	6756 (6)	4119 (9)	477 (69)	1
C(2)	3079 (8)	6793 (6)	4607 (9)	512 (78)	1
C(3)	3247 (9)	7123 (6)	5753 (10)	614 (82)	1
C(4)	2476 (11)	7426 (7)	6318 (11)	729 (100)	1
C(5)	1479 (9)	7427 (8)	5813 (13)	814 (108)	1
C(6)	1245 (9)	7096 (7)	4720 (10)	732 (95)	1
C(7)	1790 (9)	6377 (7)	3058 (11)	643 (88)	1
C(8)	5531 (8)	7120 (6)	752 (9)	492 (74)	1
C(9)	4492 (7)	7080 (6)	357 (9)	525 (77)	1
C(10)	4231 (9)	7478 (7)	-750 (10)	629 (83)	1
C(11)	4953 (11)	7861 (7)	-1308 (10)	683 (106)	1
C(12)	5969 (10)	7887 (7)	-938 (11)	682 (95)	1
C(13)	6244 (8)	7532 (6)	93 (11)	623 (89)	1
C(14)	5894 (8)	6729 (7)	1801 (10)	572 (82)	1
C(15)	1997 (9)	5606 (6)	1317 (9)	538 (97)	1
C(16)	2188 (12)	4713 (7)	1568 (11)	1021 (140)	1
C(17)	3041 (18)	4532 (13)	2506 (20)	1033 (91)	0.6458
C(17')	5148 (36)	4666 (24)	2127 (38)	1049 (172)	0.3542
C(18)	5896 (8)	5889 (7)	3483 (9)	657 (78)	1
C(19)	5895 (11)	4974 (8)	3206 (14)	1071 (129)	1
C(20)	4779 (18)	4618 (12)	3310 (18)	907 (80)	0.6458
C(20')	3463 (34)	4508 (23)	1379 (36)	960 (150)	0.3542
C(21)	4381 (20)	4670 (14)	1126 (21)	1118 (96)	0.6458
C(21')	3870 (32)	4610 (24)	3552 (35)	986 (157)	0.3542
C(1B)	3820 (10)	8590 (9)	2787 (12)	984 (44)	1
C(2B)	3769 (11)	8927 (9)	3831 (13)	1044 (45)	1
C(3B)	3829 (12)	9773 (10)	3996 (14)	1139 (49)	1
C(4B)	3941 (12)	10212 (10)	2984 (16)	1274 (55)	1
C(5B)	3983 (12)	9888 (10)	1880 (15)	1263 (54)	1
C(6B)	3914 (11)	9022 (9)	1820 (13)	1082 (46)	1

the Schiff-base aliphatic chains and were refined isotropically with their occupancy factors compelled to reach the overall value of 1.00. All other non-H atoms in the complex molecule were refined anisotropically; final refinement of 293 parameters gave $R = 0.073$, $wR = 0.077$, $S = 2.33$, weighting scheme $w = 4.9671/[\sigma^2(F_o) + 0.000752F_o^2]$; max. $\Delta/\sigma = 0.319$ for U C(17)'; all maxima in last $\Delta\rho$ map $< 0.66 \text{ e \AA}^{-3}$. Some efflorescence together with the disorder did not allow better results.

Scattering factors for neutral atoms including f' and f'' from *International Tables for X-ray Crystallography* (1974). Calculations performed with *SHELX76* (Sheldrick, 1976).

Discussion. Positional parameters and U values are given in Table 1.* A view of the structure is shown in Fig. 1. Interatomic distances and bond angles are summarized in Table 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42679 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure of SALMeDPT–Cu^{II} contains discrete molecules of the complex and benzene molecules in a 1:1 ratio. The coordination sphere around the Cu atom is distorted trigonal bipyramidal. The main deviations from the regular trigonal bipyramid are in the Cu–N(3) distance, 2.337 (9) Å [while the other four metal–donor lengths average 1.950 (8) Å], and in the bond angles. In Table 3 selected bond parameters relevant to some SALMeDPT–metal complexes are listed. The most relevant effect is the enlargement of the equatorial O(1)–Cu–O(2) angle up to 145.6 (3)°. The O(1)–M–O(2) angle is usually larger than the theoretical value of 120° in all the complexes reported in Table 3 and it increases when the metal is changed in the order Co^{II} < Fe^{II} < Ni^{II} < Cu^{II}. It seems that the O(1)–M–O(2) angle increases with the content of 3*d* electrons on the metal centre but Co^{II} does not follow this order.

The N(1)–Cu–N(3) and N(2)–Cu–N(3) angles are significantly smaller than 90° while the N(1)–Cu–N(2) angle is less than 180°. These distortions are related to the lengthening of the Cu–N(3) bond distance.

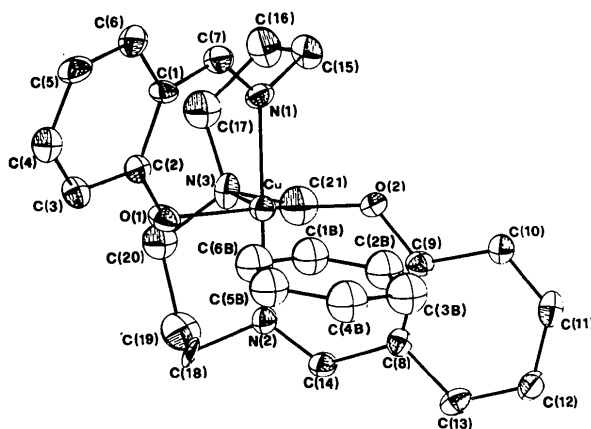


Fig. 1. ORTEP (Johnson, 1971) drawing of the title compound with the labelling scheme and ellipsoids at 30% probability. The ellipsoids relevant to C(17)', C(20)' and C(21)' are not reported for clarity.

The benzene molecule is close to the metal centre and it is almost parallel with the O(1), O(2), N(3) plane. The dihedral angle between the two planes is 11.4 (4)° while the Cu^{II} ion is 0.300 (2) Å away from the benzene plane. One of the benzene C atoms, namely C(1B), points towards the metal atom. The contact distance between the metal centre and the calculated position of the H atom on C(1B) is 2.90 Å.

Table 2. Bond distances (Å) and angles (°) with their *e.s.d.*'s

Cu–O(1)	1.950 (7)	N(3)–C(20)	1.480 (23)	N(3)–C(17)'	1.498 (44)
Cu–O(2)	1.941 (7)	N(3)–C(21)	1.517 (25)	N(3)–C(20)'	1.443 (42)
Cu–N(1)	1.951 (8)	C(1)–C(7)	1.402 (15)	N(3)–C(21)'	1.510 (41)
Cu–N(2)	1.957 (8)	C(15)–C(16)	1.533 (16)	C(8)–C(14)	1.428 (14)
Cu–N(3)	2.337 (9)	C(16)–C(17)	1.533 (24)	C(18)–C(19)	1.559 (17)
O(1)–C(2)	1.321 (11)	C(19)–C(17)'	1.615 (44)	C(19)–C(20)	1.589 (24)
N(1)–C(7)	1.309 (14)	O(2)–C(9)	1.295 (11)	C(16)–C(20)'	1.732 (43)
N(1)–C(15)	1.469 (12)	N(2)–C(14)	1.279 (12)		
N(3)–C(17)	1.479 (24)	N(2)–C(18)	1.475 (12)		
C(1)–C(2)	1.416 (13)	C(3)–C(4)	1.337 (15)	C(5)–C(6)	1.391 (17)
C(2)–C(3)	1.435 (14)	C(4)–C(5)	1.394 (17)	C(6)–C(1)	1.428 (13)
C(8)–C(9)	1.407 (13)	C(10)–C(11)	1.341 (15)	C(12)–C(13)	1.356 (15)
C(9)–C(10)	1.459 (14)	C(11)–C(12)	1.370 (16)	C(13)–C(8)	1.420 (13)
C(1B)–C(2B)	1.335 (17)	C(3B)–C(4B)	1.394 (19)	C(5B)–C(6B)	1.449 (20)
C(2B)–C(3B)	1.425 (19)	C(4B)–C(5B)	1.387 (20)	C(6B)–C(1B)	1.339 (17)
Cu–O(1)–C(2)	125.3 (6)	O(1)–Cu–N(2)	90.8 (3)		
Cu–N(1)–C(7)	123.1 (8)	O(2)–Cu–N(2)	91.7 (3)		
Cu–N(1)–C(15)	116.4 (7)	N(1)–Cu–N(2)	174.7 (4)		
C(7)–N(1)–C(15)	120.6 (9)	N(1)–Cu–N(3)	87.2 (4)		
Cu–N(3)–C(17)	106.2 (10)	N(2)–Cu–N(3)	87.6 (3)		
Cu–N(3)–C(20)	108.1 (9)	Cu–O(2)–C(9)	126.7 (6)		
Cu–N(3)–C(21)	107.6 (10)	Cu–N(2)–C(14)	125.0 (7)		
C(17)–N(3)–C(20)	108.7 (13)	Cu–N(2)–C(18)	114.7 (7)		
C(17)–N(3)–C(21)	110.1 (14)	O(2)–C(9)–C(10)	118.7 (9)		
C(20)–N(3)–C(21)	115.7 (14)	C(14)–N(2)–C(18)	120.3 (9)		
C(2)–C(1)–C(7)	122.9 (10)	Cu–N(3)–C(17)'	109.8 (16)		
C(6)–C(1)–C(7)	116.7 (10)	Cu–N(3)–C(20)'	113.8 (16)		
O(1)–C(2)–C(1)	123.0 (9)	Cu–N(3)–C(21)'	102.7 (16)		
N(1)–C(7)–C(1)	127.7 (11)	C(17)–N(3)–C(20)'	104.8 (24)		
N(1)–C(15)–C(16)	109.9 (9)	C(17)–N(3)–C(21)'	107.4 (24)		
C(15)–C(16)–C(17)	115.3 (12)	C(20)–N(3)–C(21)'	118.1 (23)		
O(1)–C(2)–C(3)	119.1 (9)	C(9)–C(8)–C(14)	120.9 (10)		
N(3)–C(17)–C(16)	116.9 (16)	C(13)–C(8)–C(14)	118.7 (10)		
C(15)–C(16)–C(20)'	108.4 (15)	O(2)–C(9)–C(8)	125.9 (10)		
N(3)–C(20)–C(16)	107.5 (26)	N(2)–C(14)–C(8)	127.9 (10)		
O(1)–Cu–O(2)	145.6 (3)	N(2)–C(18)–C(19)	110.3 (10)		
O(1)–Cu–N(3)	104.5 (3)	C(18)–C(19)–C(20)	109.8 (12)		
O(2)–Cu–N(3)	109.9 (3)	N(3)–C(20)–C(19)	112.0 (14)		
O(1)–Cu–N(1)	91.5 (3)	C(18)–C(19)–C(17)'	117.5 (17)		
O(2)–Cu–N(1)	89.1 (3)	N(3)–C(17)–C(19)	109.7 (27)		
C(1)–C(2)–C(3)	117.8 (10)	C(8)–C(9)–C(10)	115.3 (10)		
C(2)–C(3)–C(4)	121.3 (11)	C(9)–C(10)–C(11)	120.3 (11)		
C(3)–C(4)–C(5)	120.9 (12)	C(10)–C(11)–C(12)	124.6 (11)		
C(4)–C(5)–C(6)	121.5 (11)	C(11)–C(12)–C(13)	117.1 (11)		
C(5)–C(6)–C(1)	118.0 (10)	C(12)–C(13)–C(8)	122.3 (11)		
C(6)–C(1)–C(2)	120.3 (10)	C(13)–C(8)–C(9)	120.4 (10)		

Table 3. Geometrical parameters in some SALMeDPT–M^{II} complexes with parameters relevant to Cu(mbp) included for comparison [mbp = N,N'-4-azaheptane-1,7-diybis(2-hydroxy-5-methylbenzophenone iminato)]

	Fe ^a	Co(α) ^b	Co(β) ^b	Co(γ) ^c	Ni ^d	Cu	Cu(mbp) ^e
M–O(1) (Å)	1.954 (4)	1.953 (6)	1.971 (9)	1.97 (1)	1.956 (7)	1.950 (7)	1.925 (5)
M–O(2)	1.951 (3)	1.941 (6)	1.952 (8)	1.96 (1)	1.954 (7)	1.941 (7)	1.951 (5)
M–N(1)	2.096 (4)	2.058 (7)	2.069 (9)	2.05 (2)	2.017 (8)	1.951 (8)	1.983 (5)
M–N(2)	2.090 (4)	2.064 (7)	2.064 (10)	2.03 (1)	2.001 (7)	1.957 (8)	1.951 (5)
M–N(3)	2.190 (4)	2.135 (7)	2.170 (9)	2.15 (1)	2.086 (8)	2.337 (9)	2.374 (10)
O(1)–M–O(2) (°)	136.9 (2)	127.9 (3)	126.9 (3)	129.8 (4)	140.6 (3)	145.6 (3)	152.2 (3)
N(1)–M–N(2)	177.2 (2)	179.6 (2)	176.8 (4)	179.0 (5)	177.0 (3)	174.7 (4)	174.9 (3)
O(1)–M–N(3)	111.3 (2)	115.9 (3)	116.4 (4)	114.1 (5)	113.5 (3)	104.5 (3)	106.5 (3)
O(2)–M–N(3)	111.8 (2)	116.2 (3)	116.6 (4)	116.1 (5)	105.9 (3)	109.9 (3)	101.0 (3)
N(1)–M–N(3)	88.2 (2)	90.0 (3)	88.9 (4)	89.7 (6)	91.1 (3)	87.2 (4)	88.9 (3)
N(2)–M–N(3)	89.0 (2)	89.7 (3)	88.3 (4)	89.4 (6)	91.8 (3)	87.6 (3)	86.2 (3)

(a) Cini (1983); (b) Cini & Orioli (1982); (c) Zanello *et al.* (1983); (d) Di Vaira, Orioli & Sacconi (1971); (e) Freyberg, Mockler & Sinn (1976).

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trans*-Bis[*dimethylglyoximato*(1-)-*N,N'*]bis(*pyrrolidine-N*)cobalt(III) Chloride, *trans*-Chlorobis[*dimethylglyoximato*(1-)-*N,N'*](*pyrrolidine-N*)cobalt(III) and *trans*-(Benzyl)bis[*dimethylglyoximato*(1-)-*N,N'*](*pyrrolidine-N*)cobalt(III)

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Abstract. (I): $[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_9\text{N})_2]\text{Cl}$, $M_r = 466.8$, $C2/c$, $a = 18.474(4)$, $b = 12.751(1)$, $c = 9.380(1)$ Å, $\beta = 107.90(1)^\circ$, $V = 2103(1)$ Å³, $Z = 4$, $D_x = 1.48$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.01$ mm⁻¹, $F(000) = 984$, room temperature, $wR = 0.041$ for 1569 reflections. (II): $[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Cl}(\text{C}_4\text{H}_9\text{N})]$, $M_r = 395.7$, $P2_12_12_1$, $a = 9.489(3)$, $b = 12.411(4)$, $c = 14.595(4)$ Å, $V = 1719(1)$ Å³, $Z = 4$, $D_x = 1.53$ Mg m⁻³, $\text{Mo } K\alpha$, $\mu = 1.22$ mm⁻¹, $F(000) = 824$, room temperature, $wR = 0.044$ for 1329 reflections. (III): $[\text{Co}(\text{C}_7\text{H}_7)(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_9\text{N})]$, $M_r = 451.4(1)$, $P2_12_12_1$, $a = 11.546(3)$, $b = 11.724(4)$, $c = 15.694(4)$ Å, $V = 2124(1)$ Å³, $Z = 4$, $D_x = 1.41$ Mg m⁻³, $\text{Mo } K\alpha$, $\mu = 0.88$ mm⁻¹, $F(000) = 952$, room temperature, $wR = 0.039$ for 1080 reflections. Ground-state *trans* effects are observed. With the Co–N(pyr) distance in (I) as reference, the Co–N(pyr) in (II) is only slightly larger, but in (III) it is significantly elongated, in keeping with the weak σ -donor ability of the chlorine compared to the benzyl ligand. Comparison of the title compounds with other

cobaloximes shows indications of ground-state *cis* effects, namely in the correlation between the larger Co–N(axial) and the smaller Co–N(equatorial) and in the shifts of the Co atoms from the plane of the four equatorial N atoms. The possibility of a ligand-induced proton shift in (II) and (III) is discussed.

Introduction. Transformation of, for example, an octahedral complex ML_6 (M : metal; L : ligand) into ML_5X causes a change in the properties of the ligands L , whilst the substituent effects of X on L are different for *trans*- and *cis*-positioned ligands L relative to X . Such *cis* and *trans* interactions influence ground-state properties as well as thermodynamic and kinetic characteristics. Unfortunately there is an excessive number of terms used in the literature to correlate the mutual influence of ligands on the properties concerned. We will follow the recommendations of Buchler, Kokisch & Smith (1978) and adhere to the terminology used by Hill, Pratt & Williams (see e.g. Philips & Williams, 1966), i.e. we will use the term ground-state *trans/cis* effect in connection with geometrical and spectroscopic properties.

Cobaloximes – $\text{Co}(\text{Hdmg})_2\text{LX}$, with Hdmg the monoanion of dimethylglyoxime – are studied because they can be considered as model compounds for vitamin B_{12} and because by analogy with vitamin B_{12}

* Dimethylglyoxime is 2,3-butanedione dioxime.

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