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Transition Metal Complexes with New Acyclic Schiff Bases

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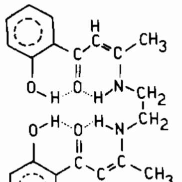
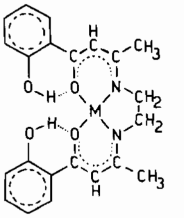
New acyclic Schiff bases derived from the condensation of o*-methoxyphenylbutane-1,3-dione or* o*-methoxyphenylpentane-1,3-dione with ethylenediamine have been prepared and characterized and mononuclear copper(II), nickel(II) and vanadyl(IV) complexes of these ligands have been synthesized. The crystal structure of the nickel complex with the latter ligand has been determined from X-ray data. The crystals are triclinic, space group* $P\bar{1}$, *with* a = *12.27(1),* b = *11.40(1),* c = *8.50(1)* Å, α = *98.2(2),* β = *95.5(2), and* γ = *95.6(2)°. The metal ion is bonded to the inner* N_2O_2 *donor set of the ligand and is approximately square planar.*

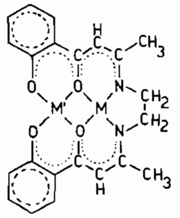
Introduction

The area of homo- and hetero-dinuclear complexes has seen extensive growth, stimulated by interest in fields as metalloenzymes, homogeneous catalysis, electrical conductance and magnetic exchange processes, and has been comprehensively reviewed [1–4]. We have recently reported [5–9] the preparation of the ligand:

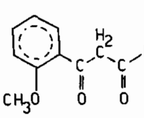


and the physico-chemical properties of mono and binuclear complexes of the type

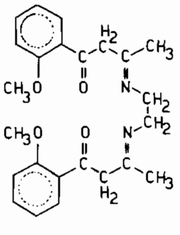




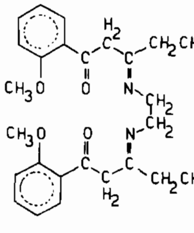
We have now synthesized two new β-diketones (I)



and a number of complexes obtained by interaction of various metal ions with the corresponding related Schiff bases H_2L_A and H_2L_B.



L_A



L_B

The crystal structure of NiL_B has been also determined by X-ray methods.

Experimental

The β-diketones (I) were prepared by the method of Wittig [10] and their purity was checked by elemental analysis and ir data. Their preparation involved the condensation of *o*-methoxyacetophenone with ethylacetate or ethylpropionate in the presence of Na under reflux; *o*-methoxyphenylbutane-1,3-dione is a pale yellow solid; m.p. 36°; *o*-methoxyphenylpentane-1,3-dione is a yellow oil which was purified by extraction from water with Et_2O. The ir spectra show the C=O stretching modes at about 1710 cm^{-1} and those of $C\underline{\cdots}O + C\underline{\cdots}C$ at 1603 cm^{-1}.

The Schiff bases H_2L_A and H_2L_B were obtained by condensation of the appropriate β-diketone with ethylenediamine in boiling ethanol. Their formulation is supported by analytical and spectral data. The

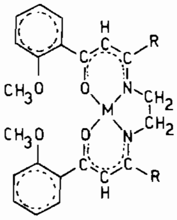
TABLE I. Elemental Analyses.

Compound		%C	%H	%N
H_2L_A	calc.	70.56	6.90	6.85
	found	70.73	6.73	6.53
H_2L_B	calc.	71.52	7.38	6.42
	found	71.80	7.53	6.71
$VOL_A(H_2O)$	calc.	58.66	5.74	5.70
	found	59.02	5.43	6.10
$VOL_B(H_2O)$	calc.	60.17	6.21	5.39
	found	60.33	6.30	5.60
CuL_A	calc.	61.37	5.57	5.96
	found	60.80	5.50	5.78
CuL_B	calc.	62.69	6.07	5.62
	found	62.94	5.84	5.71
NiL_A	calc.	61.96	5.63	6.02
	found	61.60	5.30	6.06
NiL_B	calc.	63.30	6.13	5.68
	found	63.15	6.32	5.83

TABLE II. Crystal Data for NiL_B.

$C_{26}H_{28}N_2O_4Ni$	FW 500.7
Crystal description	red-brown prisms
System	triclinic
General positions	±(x, y, z)
Cell dimensions	$a = 12.27(2)$ Å
	$b = 11.40(2)$ Å
	$c = 8.50(1)$ Å
	$\alpha = 98.18(5)^\circ$
	$\beta = 95.56(5)^\circ$
	$\gamma = 95.58(5)^\circ$
Volume	1163 Å^3
Density	obs 1.43 g cm^{-3} (flotation)
	calcd 1.43 g cm^{-3} for $Z = 2$
μ(MoKα)	8.7 cm^{-1}

ir spectra show a band at about 1600 cm^{-1} ($C\overset{\cdots}{-}O$ + $C\overset{\cdots}{-}C$) and a band at 1510 cm^{-1} (C–N). No bands in the range 1800–1700 cm^{-1} are observed, in accordance with the absence of free carbonyl groups. Mononuclear complexes of the type ML_A and ML_B (II) were prepared by reaction of equimolar ratios



of the preformed Schiff bases with nickel(II), copper(II), and vanadyl(IV) acetate in hot methanolic solution in the presence of LiOH. The formulation of the compounds is supported by analytical (Table I) and physico-chemical data. The NiL_A and NiL_B complexes are diamagnetic.

Their electronic spectra show a single band at about 580 mμ which is comparable with that found in a similar complex [6]. The ir spectra do not show the νC=N band, but give bands at 1595 cm^{-1} which are attributed to $\nu C\overset{\cdots}{-}O$ and $\nu C\overset{\cdots}{-}C$, and a band at 1510 cm^{-1} due to the stretching of a metal coordinated C–N, strongly suggesting that the metal ion is square planar coordinated in the N_2O_2 coordination site. In a previous investigation [6] using a very similar ligand and an excess of nickel(II) acetate, the formation of homodinuclear chelate has been reported; we have examined the ability of the inside N_2O_2 and of the outside O_2O_2 site to coordinate metal ions: the outside O_2O_2 donor set has shown a very low tendency to coordinate a second metal ion.

The ir spectra show peaks at 1991 and 1585 cm^{-1} (νC–O + C–C) and 1505 cm^{-1} (νC–N) for CuL_A and at 1600 cm^{-1} (νC–O + C–C) for VOL_B. In addition a stretching absorption at 980 cm^{-1}, due to the V=O group, is present in VOL_A. The values of magnetic moments at room temperature correspond to one unpaired electron.

Attempts to prepare homo- or hetero-binuclear complexes of transition metal ions under a variety of conditions failed; in any case the mononuclear complex was recovered from the reaction mixture. Only with alkaline earth or actinide ions does a reaction occur giving well defined compounds.

Ir spectra were recorded on a Perkin-Elmer 621 spectrophotometer using KBr discs; electronic spectra were recorded in Nujol mulls using a Cary 14 spectrophotometer; magnetic susceptibilities were measured by the Gouy method using a Brucker–Sartorius instrument. The apparatus was calibrated with $Ni(en)_3(ClO_4)_2$. The diamagnetic corrections were calculated from Pascal's constants.

X-ray Data

Crystals of NiL_B suitable for the X-ray analysis have been obtained by recrystallization from methanol.

A prismatic crystal of approximate dimensions 0.10 × 0.12 × 0.17 mm was mounted on a glass fibre with epoxy adhesive. All the X-ray experimental work was performed using a Philips PW 1100 single crystal diffractometer with graphite monochromated MoKα radiation (λ = 0.7107 Å). The unit cell parameters were obtained by a least-squares refinement of 25 angular settings carefully determined. Crystal data are summarized in Table II. A total of 4096 reflections were measured within $2^\circ < \theta < 25^\circ$ with a scan rate of 2° in 2θ min^{-1}.

TABLE III. Fractional Coordinates ($\times 10^4$) with Estimated Standard Deviations.

Atom	x	y	z	Atom	x	y	z
Ni	1200(2)	196(3)	2679(5)	C(11)	4513(24)	−1116(27)	2343(41)
O(1)	4154(14)	−2020(21)	6200(24)	C(12)	4778(31)	−2118(34)	7665(50)
O(2)	2542(18)	−253(18)	2985(26)	C(13)	−429(26)	1637(32)	1534(45)
O(3)	1959(13)	1624(15)	2325(27)	C(14)	−1644(22)	1775(25)	1062(36)
O(4)	2380(15)	4055(17)	4695(30)	C(15)	−1870(28)	2937(31)	464(46)
N(1)	490(16)	−1180(21)	3241(32)	C(16)	362(22)	2578(24)	1559(36)
N(2)	−233(19)	604(23)	2027(41)	C(17)	1554(22)	2544(24)	1940(36)
C(1)	950(19)	−2022(23)	3933(33)	C(18)	2358(17)	3564(20)	1941(30)
C(2)	304(21)	−3123(23)	4397(35)	C(19)	2802(21)	4285(23)	3322(35)
C(3)	117(23)	−4014(26)	3051(38)	C(20)	3647(18)	5277(20)	3365(31)
C(4)	2124(21)	−2052(24)	4195(35)	C(21)	4000(20)	5418(22)	1882(33)
C(5)	2850(20)	−1164(23)	3602(34)	C(22)	3614(19)	4744(21)	449(32)
C(6)	4117(21)	−1280(23)	3683(37)	C(23)	2743(25)	3790(28)	430(40)
C(7)	4675(20)	−1715(22)	5005(36)	C(24)	2852(24)	4741(27)	6242(41)
C(8)	5822(22)	−1876(25)	4847(37)	C(25)	−1094(23)	−414(26)	2077(38)
C(9)	6199(25)	−1560(28)	3358(41)	C(26)	−745(21)	−1192(24)	3149(35)
C(10)	5697(21)	−1252(24)	2158(35)				

Thermal parameters ($\times 10^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.6	1.8	3.8	0.5	0.7	2.1
O(1)	4.3	15.9	4.3	6.5	0.8	6.2
O(2)	2.4	6.8	9.1	1.7	0.1	4.6
O(3)	2.7	3.4	11.1	2.8	0.2	2.7
O(4)	4.9	6.5	11.9	3.8	2.4	2.7
N(1)	2.3	5.9	8.1	−3.0	1.0	0.8
N(2)	3.6	5.2	15.1	0.7	2.4	3.2

Atom	U	Atom	U
C(1)	3.5	C(14)	4.8
C(2)	4.7	C(15)	8.4
C(3)	5.8	C(16)	4.5
C(4)	4.3	C(17)	4.9
C(5)	3.8	C(18)	2.7
C(6)	4.3	C(19)	4.0
C(7)	4.1	C(20)	3.4
C(8)	5.6	C(21)	4.0
C(9)	6.4	C(22)	3.8
C(10)	4.6	C(23)	6.7
C(11)	6.2	C(24)	6.2
C(12)	9.4	C(25)	5.3
C(13)	6.8	C(26)	4.9

Of these, only 1198 with non zero intensity values (*i.e.*, with $F_o^2 > 2\sigma(F_o^2)$) were used in the structure determination. The very high number of non observed reflections and the relatively low intensities of the observed ones are probably an indication of the poor quality of the crystals, perhaps a low degree of crystallinity of the compound, as seemed to be successively confirmed during the refinement by the relatively high values of the atom temperature factors. However two standard reflections, which were monitored every 100 reflections, were constant within counting statistics, showing no significant crystal decomposition during irradiation.

All data were corrected for Lp but not for absorption. The asymmetric unit comprises one molecule of the compound. An origin-removed Patterson synthesis showed the position of the Ni atom, and all other non-hydrogen atoms were successively located from difference syntheses. Refinement of scale factor, positional and isotropic

TABLE IV. Distances.

Bond distances (Å) with estimated standard deviations			
Coordination			
Ni–O(2)	1.78(2)	Ni–N(1)	1.86(2)
Ni–O(3)	1.87(2)	Ni–N(2)	1.91(2)
Ligand			
N(1)–C(1)	1.34(4)	N(2)–C(13)	1.34(4)
N(1)–C(26)	1.51(3)	N(2)–C(25)	1.50(4)
C(1)–C(2)	1.54(4)	C(13)–C(14)	1.53(4)
C(1)–C(4)	1.44(3)	C(13)–C(16)	1.37(4)
C(2)–C(3)	1.40(4)	C(14)–C(15)	1.52(5)
C(4)–C(5)	1.46(4)	C(16)–C(17)	1.47(4)
C(5)–C(6)	1.57(4)	C(17)–C(18)	1.45(3)
O(1)–C(7)	1.32(4)	O(4)–C(19)	1.37(4)
O(1)–C(12)	1.42(4)	O(4)–C(24)	1.46(4)
O(2)–C(5)	1.30(4)	O(3)–C(17)	1.27(4)
C(25)–C(26)	1.42(4)		
Mean C–C in phenyl 1.40 Å			
Shortest contact distances (Å)			
O(2)···O(3)	2.44(2)	O(3)···N(2)	2.79(2)
O(2)···N(1)	2.68(2)	N(1)···N(2)	2.60(2)

thermal parameters converged to R = 10.3%. Further refinement including anisotropic temperature factors for nickel, oxygen and nitrogen atoms converged at R = 9.8% when the largest parameter shift in the last cycle was 0.1 σ. A final difference Fourier synthesis showed no significant residuals. Hydrogen atoms were not introduced because of the difficulty in determining experimentally their positions. Throughout the refinement, w = 1 was assigned to the observed structure amplitudes. Scattering factors were those of Cromer and Waber [11], the anomalous dispersion correction was applied for the nickel atom [12]. All calculations were done using the X-ray '73 program system [13]. Final atomic positions are listed in Table III. Bond distances and angles are reported in Tables IV and V.

Information concerning selected molecular planes and dihedral angles is given in Table VI.

Description of the Structure of NiL_B

The crystal consists of monomeric NiL_B units as shown in Fig. 1, in which the structure is projected along the *c* axis of the cell. The nickel atom, which is retained in the inner N_2O_2 chamber, is four coordinated and approximately square planar. However the O–Ni–N angles (172 and 174°) significantly differ from linearity, and the four bonded atoms are alternatively displaced by +0.1 Å and –0.1 Å from the mean plane (Table VI), so that the coordination geometry is slightly distorted toward the tetrahedral configuration. Within the limits of the errors bond distances and angles substantially agree with those found in other nickel complexes, and in particular in $NiCu(aapen)H_2O$ where aapen is a parent ligand. The main difference between the two

TABLE V. Bond Angles (°) with Estimated Standard Deviations.[a]

Coordination			
O(2)–Ni–O(3)	84(1)	N(1)–Ni–N(2)	87(1)
O(2)–Ni–N(1)	95(1)	O(3)–Ni–N(2)	95(1)
O(2)–N(1)–N(2)	172(1)	O(3)–Ni–N(1)	174(1)
Ligand			
Ni–O(2)–C(5)	129(2)	Ni–O(3)–C(17)	128(2)
Ni–N(1)–C(1)	128(2)	Ni–N(2)–C(13)	124(2)
Ni–N(1)–C(26)	113(2)	Ni–N(2)–C(25)	110(2)
C(1)–N(1)–C(26)	118(2)	C(13)–N(2)–C(25)	125(2)
N(1)–C(1)–C(2)	124(2)	N(2)–C(13)–C(14)	116(3)
N(1)–C(1)–C(4)	123(2)	N(2)–C(13)–C(16)	124(2)
C(1)–C(2)–C(3)	108(2)	C(13)–C(14)–C(15)	116(2)
C(2)–C(1)–C(4)	112(2)	C(14)–C(13)–C(16)	120(3)
C(1)–C(4)–C(5)	119(2)	C(13)–C(16)–C(17)	125(3)
C(4)–C(5)–O(2)	125(2)	C(16)–C(17)–O(3)	123(2)
C(4)–C(5)–C(6)	119(2)	C(16)–C(17)–C(18)	123(2)
O(2)–C(5)–C(6)	115(2)	O(3)–C(17)–C(18)	115(2)
C(7)–O(1)–C(12)	119(2)	C(19)–O(4)–C(24)	120(2)
N(1)–C(26)–C(25)	109(2)	N(2)–C(25)–C(26)	112(2)

[a] Bond angles of the phenylene rings are between 117 and 123 degrees with a mean of 120 degrees.

TABLE VI. Least-squares Planes and Distances (Å) of Atoms from the Planes. The equation of a plane is PX + QY + RZ = S with coordinates referred to the crystallographic axes.

Plane I	O(2), O(3), N(1), N(2). $-1.656X + 3.391Y + 7.705Z = 1.908$ [O(2) −0.11; O(3) 0.11; N(1) 0.11; N(2) −0.10; Ni[a] 0.02]
Plane II	C(6)–C(11) $1.672X + 10.080Y + 2.224Z = 0.179$ [C(6) 0.04; C(7) −0.01; C(8) −0.02; C(9) 0.03; C(10) −0.01; C(11) −0.03]
Plane III	C(18)–C(23) $9.230X - 8.149Y + 1.296Z = -0.483$ [C(18) 0.01; C(19) 0.01; C(20) −0.01; C(21) 0.00; C(22) 0.01; C(23) −0.02]

Angles between the planes

Planes	Angle (°)
I–II	51
I–III	81
II–III	65

[a] Atom not used in the plane calculation.

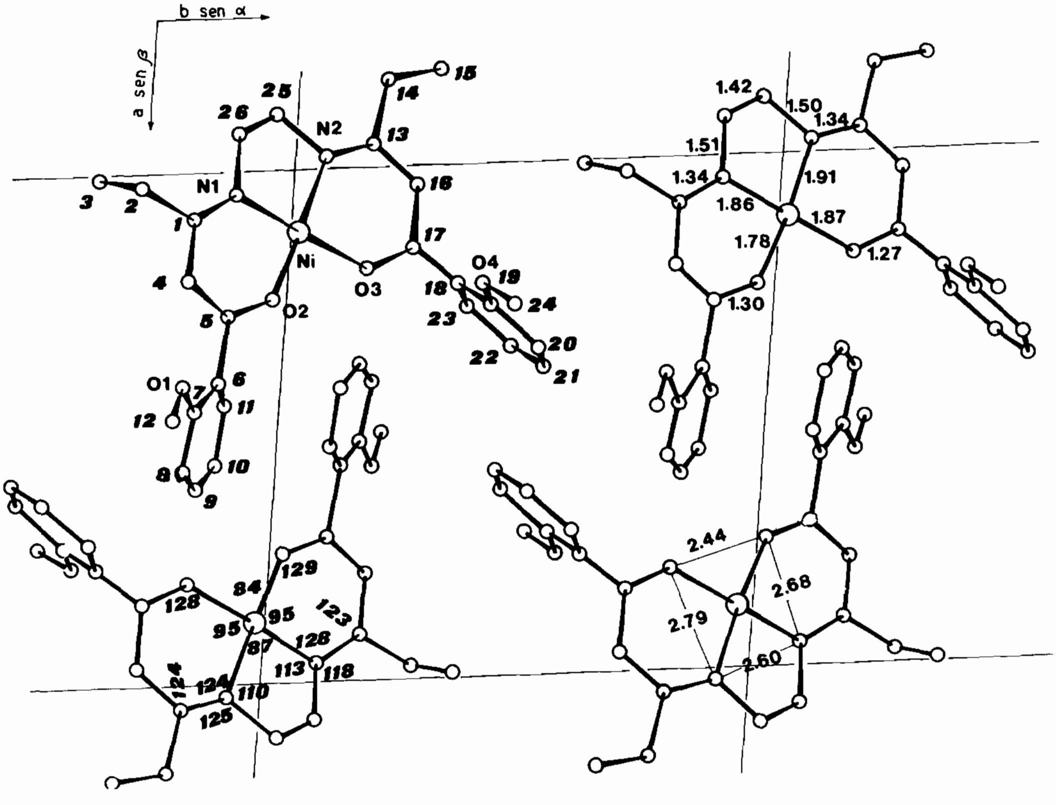


Fig. 1. Projection of the structure of NiL_B along the *c* axis.

compounds lies, apart from the chemical formula, in the fact that the ligand is essentially planar in the binuclear $NiCu(aapen)H_2O$, whereas the phenylene groups are considerably tilted to the base plane in NiL_B, with torsion angles of 51 and 81 degrees about the respective C–C bonds. Because both methoxy groups lie on the same side of the base plane and both ethyl groups lie on the opposite side of the same plane, the molecule has approximately the Cs group symmetry.

Several contacts in the range 3.5–3.9 Å which could play an active role in holding together the molecules in the direction of the *b* axis are present between the C(6)–C(11) ring at x, y, z and the corresponding ring at $1 - x, \bar{y}, 1 - z$. Similar contact distances in the *a* axis direction exist between the terminal atoms of the second ring and the corresponding atoms at $1 - x, 1 - y, \bar{z}$. Finally atoms of the equatorial plane at x, y, z make several contacts in the range 3.7–4.2 Å in the direction of the *c* axis with those of molecules at $\bar{x}, \bar{y}, \bar{z}$ and $\bar{x}, \bar{y}, 1 - z$.

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