Inorganica Chimica Acta, 32 (1979) 53–58

Alkoxy-bridged Complexes of Copper(II) and NIckel(II) with Schiff Bases of Alcoholamines – Including Effects of Structural Distortion on the Electronic Spectra of Six-coordinate Nickel(II) Complexes

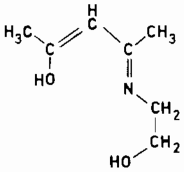
A. E. LANDERS and D. J. PHILLIPS

The School of Chemistry, The University of New South Wales, Kensington, NSW, Australia, 2033
Received May 19, 1978

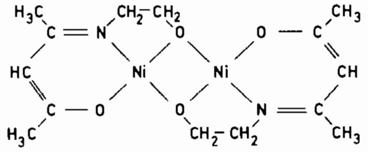
This paper describes the copper(II) complexes of the Schiff bases (eiLH_2) of 2-aminoethanol with acetylacetone, benzoylacetone, dibenzoylmethane and ethyl acetoacetate, together with the copper(II) complexes of the Schiff bases (piLH_2) of 3-amino-1-propanol with the above diones. Nickel(II) complexes are also described, using some eiLH_2 Schiff bases incorporating the first three diones. Measurements of molecular weight, mass and visible spectra and magnetic measurements down to ca. *90K, are reported. The complexes* $[Cu(eiL)]_4$ *appear to be tetrameric, probably with oxygen-bridged cubane structures; they have room temperature* μ_{eff} *values of* ca. *1.9 B.M. and are weakly ferromagnetic. The complexes* $[Cu(piL)]_2$ *and* $[Ni(eiL)]_2$ *appear to have planar dimeric structures; the copper complexes have magnetic moments of* ca. *0.6 B.M. and the nickel complexes are diamagnetic. Some paramagnetic alcohol adducts of the type* $[Ni(eiL)ROH]_4$ *(R = Me, Et,* n-*Pr,* n-*Bu) are assigned tetrameric cubane structures. These alcoholate complexes have* μ_{eff} *values of* ca. *3.3 B.M. at room temperature, and appear to be weakly ferromagnetic. The reflectance electronic spectra of the* $[Ni(eiL)ROH]_4$ *complexes are unusual in that they give evidence of marked tetragonal distortion, which appears to be produced by a structural distortion in the coordination environment of the nickel(II) ions. These spectra are compared with those of other, less distorted, nickel(II) tetramers.*

Introduction

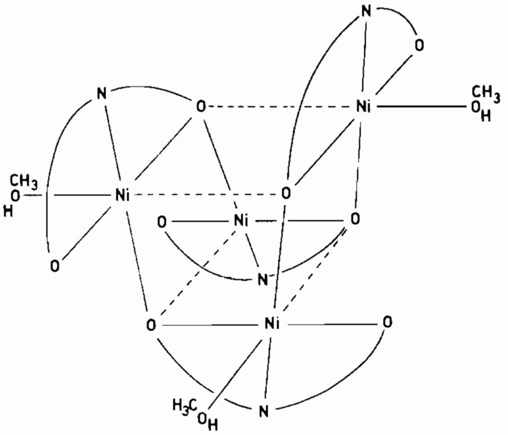
Aminoalcohol ligands are a fruitful source of oxygen-bridged metal complexes, with a variety of



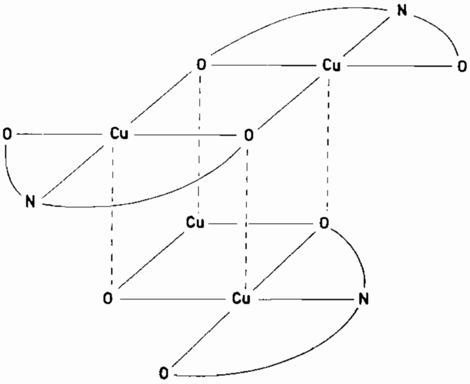
(I) The ligand $eiaH_2$.



(II) Structure of $[Ni(eia)]_2$.



(III) Simplified structure of $[Ni(eia)CH_3OH]_4$ (dashes indicate elongated bonds).



(IV) Simplified structure of α-$[Cu(eia)]_4$ (dashes indicate elongated bonds, one eia unit is omitted).

TABLE I. Analytical and Magnetic Data of the Complexes.

Compound	Analyses %				μ_{eff} (B.M.)	Temp. (K)	θ(K)[b]
	Calculated and Found						
	C	H	N	M			
α-[Cu(eia)]$_4$	41.1	5.4	6.8	–	1.86[c]	300	–20
	41.1	5.5	6.8	–	1.73[c]	80	
β-[Cu(eia)]$_4$	41.1	5.4	6.8	31.0	1.89	297	20
	40.9	5.5	6.8	31.2	2.05	86	
[Cu(eiba)]$_4$	54.0	4.9	5.2	23.8	1.80	303	25
	53.7	4.9	5.1	23.8	1.98	86	
[Cu(eidb)]$_4$[a]	62.1	4.6	4.3	19.3	1.92	295	10
	62.3	4.6	4.1	19.0	1.95	86	
[Cu(eiet)]$_4$[a]	40.9	5.6	6.0	27.1	1.93	294	10
	40.7	5.5	7.7	27.1	2.01	86	
[Cu(pia)]$_2$	43.9	6.0	6.4	–	0.24	293	
	44.2	5.8	6.3	–			
[Cu(piba)]$_2$[a]	55.6	5.4	5.0	22.6	0.66	293	
	55.5	5.5	4.9	22.3			
[Cu(pidb)]$_2$·H_2O[a]	61.4	5.2	4.0	18.1	0.82	293	
	61.8	5.1	3.7	18.3			
[Cu(piet)]$_2$[a]	43.4	6.1	5.6	25.5	0.28	293	
	42.7	5.7	5.6	25.6			
[Ni(eia)]$_2$	42.1	5.5	7.0	29.4	diamagnetic		
	42.1	5.5	6.8	29.2			
[Ni(eiba)]$_2$	55.0	5.0	5.3	22.4	diamagnetic		
	54.5	4.9	5.0	22.7			
[Ni(eidb)]$_2$[a]	63.0	4.7	4.3	18.1	diamagnetic		
	63.7	4.9	4.7	18.0			
[Ni(eia)CH_3OH]$_4$	41.4	6.5	6.1	–	3.29	288	12
	41.0	6.4	6.1	–	3.41	101	
[Ni(eia)*n*-C_3H_7OH]$_4$[a]	46.2	7.4	5.4	22.6	3.29	293	12
	46.1	7.4	5.7	22.9	3.49	86	
[Ni(eia)*n*-C_4H_9OH]$_4$[a]	48.3	7.7	5.1	–	3.34	288	7
	48.4	7.7	5.5	–	3.43	83	
[Ni(eiba)CH_3OH]$_4$	53.1	5.8	4.8	20.0	3.28	293	22
	52.5	5.7	4.6	19.9	3.47	101	
[Ni(eiba)C_2H_5OH]$_4$	54.5	6.2	4.5	–	3.25	293	17
	54.3	5.9	4.9	–	3.47	86	
[Ni(eidb)CH_3OH]$_4$[a]	60.7	5.4	3.9	–	3.28	293	20
	60.8	5.3	3.7	–	3.59	86	
[Ni(acac)(CH_3O)(CH_3OH)]$_4$	38.0	6.3	–	–	3.31[d]	296	25
	37.4	6.5	–	–	3.72[d]	84	
[Ni(sal)(CH_3O)(C_2H_5OH)]$_4$	46.7	5.5	–	–	3.30[e]	302	30
	46.7	5.4	–	–	3.77[e]	89	

[a] New compounds. [b] The θ values are all estimated from data above 80 K, taking the Curie–Weiss law as $\chi_A^{-1} \propto (T - \theta)$.
[c] From reference 7. [d] From reference 10. [e] From reference 9.

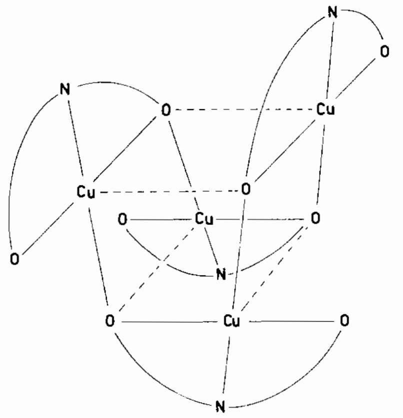
structures. For example, N-substituted 2-aminoethanol complexes, of the type [Cu(II)(ligand)X]$_n$ (X = halide or pseudohalide), yield complexes with dimeric, polymeric and two types of tetrameric structures [1]. The Schiff bases of aminoalcohols with diketones are similarly productive. The Schiff base eiaH_2, (I), of 2-aminoethanol with acetylacetone produces a diamagnetic nickel(II) complex, [Ni(eia)]$_2$, with the dimeric structure (II) [3]. This complex yields a methanol adduct, [Ni(eia)(CH_3OH)]$_4$, which is paramagnetic [2] with the tetrameric cubane structure (III) [4]. With copper(II), eiaH_2 produces two forms of tetrameric [Cu(eia)]$_4$. The complex α-[Cu(eia)]$_4$ has the cubane structure (IV) and is antiferromagnetic [5–7]. The β-isomer, isolated as the benzene solvate, β-[Cu(eia)]$_4$·2C_6H_6, has the cubane structure (V) and is ferromagnetic [7, 8]. The benzene is loosely held in the lattice, readily being lost to give a ferromagnetic form of [Cu(eia)]$_4$, which is considered to have the β-[Cu-

TABLE II. Reflectance Spectra of the Copper and Unsolvated Nickel Complexes.

Compound	Absorption Maxima (cm^{-1})
α-[Cu(eia)]$_4$	14500 br
β-[Cu(eia)]$_4$	15800
[Cu(eiba)]$_4$	15800
[Cu(eidb)]$_4$	16100
[Cu(eiet)]$_4$	15700
[Cu(pia)]$_2$	17900
[Cu(piba)]$_2$	17700
[Cu(pidb)]$_2$·H_2O	17600
[Cu(piet)]$_2$	17600
[Ni(eia)]$_2$	*ca.* 20000 br
[Ni(eiba)]$_2$	*ca.* 21000 br
[Ni(eidb)]$_2$	*ca.* 21000 br

TABLE III. Mass Spectral Data.

Compound	Most Intense Peak in Molecular Ion Cluster (m/e)	Calculated Mass Number of Most Common Isotope
[Cu(pia)]$_2$	436	436
[Cu(piba)]$_2$	560	560
[Cu(piet)]$_2$	496	496
[Ni(eia)]$_2$	398	398
[Ni(eiba)]$_2$	522	522
[Ni(eidb)]$_2$	646	646



(V) Simplified structure of β-[Cu(eia)]$_4$ (dashes indicate elongated bonds).

(eia)]$_4$ structure [8]. This ferromagnetic form of [Cu(eia)]$_4$ may also be made [8] directly from ligand and copper(II) acetate, by Jäger's method [2]

The Schiff base piaH$_2$, of 3-amino-1-propanol with acetylacetone, yields a dimeric copper(II) complex, [Cu(pia)]$_2$, with structure similar to (II), in contrast to the copper tetramers produced by eiaH$_2$ [5].

No spectral data have been reported on the above complexes, and only for the [Cu(eia)]$_4$ system have magnetic measurements been made over a temperature range [6, 7]. We have, therefore, made a detailed study of complexes of these ligands, using an extended range of diones because of the dependence of the structures of these complexes on the detailed nature of the ligands.

Results and Discussion

The ligands discussed in this paper are the Schiff bases (eiLH$_2$) of 2-aminoethanol with acetylacetone, benzoylacetone, dibenzoylmethane and ethyl acetoacetate (eiaH$_2$, eibaH$_2$, eidbH$_2$ and eietH$_2$, respectively) and the Schiff bases (piLH$_2$) of 3-amino-1-propanol with acetylacetone, benzoylacetone, dibenzoylmethane and ethyl acetoacetate (piaH$_2$, pibaH$_2$, pidbH$_2$ and pietH$_2$, respectively). The complexes of these ligands are listed, together with analytical and magnetic data in Table I, with reflectance electronic spectral data in Tables II and IV, and with mass spectral data in Table III.

It can be seen that the physical properties of each complex, whose crystal structure has been determined, are very similar to the physical properties of related complexes of unknown structure. The first conclusion is, therefore, that the structures of the complexes are unaffected by changes in the substituents on the dione entities in the ligands. This contrasts with the marked effect of changing from a dimethylene to trimethylene linkage in the imino-alcohol entities in the complexes [5] [Cu(eia)]$_4$ and [Cu(pia)]$_2$. In other words, Schiff base ligands incorporating 2-aminoethanol produce diamagnetic [Ni(eiL)]$_2$ complexes, with structure (II), and paramagnetic [Ni(eiL)(ROH)]$_4$ compounds with structure (III). The ferromagnetic [Cu(eil)]$_4$ complexes all appear to have the β-cubane structure (V), whereas the [Cu(piL)]$_2$ complexes, using ligands incorporating 3-amino-1-propanol have dimeric structures similar to (II).

Molecular weight measurements in benzene, by vapour pressure osmometry, confirm that [Cu(eiet)]$_4$ is tetrameric (molecular weight: calculated, 939; found 935) and that [Cu(piet)]$_2$ is dimeric (molecular weight: calculated, 498; found, 488). Measurements were not possible on other compounds of unknown structure, because of low solubilities or stabilities. Attempts to obtain molecular weights from mass spectra were unsuccessful for the tetrameric copper(II) complexes and for [Cu(pidb)]$_2$·H_2O because of decomposition, however, mass spectra were obtained, with molecular ions corresponding to dimeric structures, for the remaining complexes of the type [Cu(piL)]$_2$ and for the nickel complexes, [Ni(eiL)]$_2$. The spectra of the copper complexes,

TABLE IV. Reflectance Spectral Data for Paramagnetic Nickel(II) Complexes (cm^{-1}).

Compound	Bands (ν_{max})			B^c	ν_b^{c} (calculated)	ν_c^{c} (calculated)
	ν_a	ν_b	ν_c			
[Ni(eia)CH$_3$OH]$_4$	6800sh, 7900m	12300s	17000s	373	11450	17850
[Ni(eia)n-C$_3$H$_7$OH]$_4$	7800m	12200s	16900s	380	11400	17700
[Ni(eia)n-C$_4$H$_9$OH]$_4$	7800m	12000s	16800s	360	11250	17550
[Ni(eiba)CH$_3$OH]$_4$	8000m	12000s	17000s	333	11300	17700
[Ni(eiba)C$_2$H$_5$OH]$_4$	7800m	12100s	17000s	380	11400	17700
[Ni(eidb)CH$_3$OH]$_4$	7900m	12000s	17000s	353	11300	17700
[Ni(CH$_3$OH)$_6$](ClO$_4$)$_2$^{a,b}	8450	13800	25000	897	14020	24800
[Ni((CH$_3$)$_2$SO)$_6$](ClO$_4$)$_2$^{b}	8050	13250	24250	890	13400	24100
[Ni(sal)(CH$_3$O)(C$_2$H$_5$OH)]$_4$	9000	15600	25000	907	14850	25750
[Ni(acac)(CH$_3$O)(CH$_3$OH)]$_4$	9000	15400	*ca.* 25500sh	–	–	–

^{a}Solution spectrum. ^{b}Spectra from reference 12. ^{c}B was calculated from the relationship $15B = \nu_c + \nu_b - 3\nu_a$. The calculated values of ν_b and ν_c were then obtained from the secular determinant [11] for octahedral nickel(II), assuming that 10 Dq was ν_a.

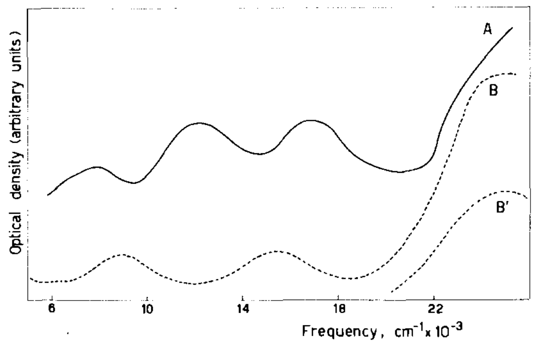


Figure. Diffuse reflectance spectra: (A), [Ni(eia)n-C$_3$H$_7$OH]$_4$; (B), (B'), [Ni(sal)(CH$_3$O)(C$_2$H$_5$OH)]$_4$. Spectrum B' was recorded on a Unicam SP500 spectrophotometer, the remainder on a Zeiss PMQII spectrophotometer.

[Cu(piL)]$_2$, gave the isotopic cluster patterns of dicopper species, namely three peaks with relative intensities of approximately 5, 4 and 1, in order of increasing m/e values, spaced at 2 m/e value increments. Likewise, the mass spectra of the nickel complexes gave analogous isotopic cluster patterns with relative intensities of approximately 9, 7 and 2.5, corresponding to di-nickel species (see Table III).

Our magnetic data show that the nickel(II) cubane alcoholates, [Ni(eiL)ROH]$_4$, are ferromagnetic. This agrees with the ferromagnetism found for the analogous cubane compounds [Ni(sal)(CH$_3$O)(C$_2$H$_5$OH)]$_4$ and [Ni(acac)(CH$_3$O)(CH$_3$OH)]$_4$ (sal and acac are the anions of salicyaldehyde and acetylacetone) [6, 9, 10]. These nickel tetramers all have a β-cubane arrangement [9, 10] (analogous to that of β-[Cu(eia)]$_4$). Because of this β-cubane structure, the formation of the [Ni(eiL)ROH]$_4$ complexes from the planar dimers [Ni(eiL)]$_2$, by reaction with alcohols, must involve rearrangement of the coordination by the eiL ligands, since a simple positioning of one undistorted [Ni(eiL)]$_2$ unit above another would lead to the α-cubane structure. In view of this rearrangement, it may be significant that the ease of preparation of these alcoholates decreases as the substituents on the diketones become more bulky. No alcohol failed to yield an adduct with [Ni(eia)]$_2$, whereas methanol was the only alcohol to produce an adduct with [Ni(eidb)]$_2$.

Bertrand and co-workers [4] showed that the coordination about each nickel in [Ni(eia)(CH$_3$OH]$_4$ was a tetragonally distorted octahedron. The three donor atoms of the coordinated ligand, and one bridging alkoxide from an adjacent ligand form the basal plane with short distances (1.93–2.06 Å). The methanol oxygen and the other alkoxide oxygen occupy the axial positions with longer distances (2.11–2.25 Å). In contrast, the NiO$_6$ coordination structures, in the related tetramers [Ni(sal)(CH$_3$O)(C$_2$H$_5$OH)]$_4$ and [Ni(acac)(CH$_3$O)(CH$_3$OH)]$_4$, are less distorted, and closer to being regular octahedral [9, 10]. We felt it of interest to see how sensitive the electronic spectra are to the distortions in these complexes. The reflectance spectra of the paramagnetic nickel(II) complexes are shown in Table IV, with derived parameters, and in the Figure.

The spectra of the [Ni(eia)ROH]$_4$ complexes superficially resemble those of octahedral nickel(II). The spectra consist of three bands ν_a, ν_b, and ν_c at *ca.* 8,000, 12,000 and 17,000 cm^{-1}, which may be assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$, $^3T_{1g}(\nu_2)$, and $^3T_{1g}(P)(\nu_3)$ of octahedral nickel(II). With this assignment, the calculated frequencies of ν_b and ν_c are moderately close to the observed values. This assignment is, however, rejected for the following reasons. The third band ν_c, at *ca*, 17,000 cm^{-1}, has a much lower frequency than is usually found for ν_3 of octahedral nickel(II) [11, 12]. The lowest value of ν_3, which we have found for six-coordinate nickel(II), is 20,600 cm^{-1}. Furthermore, the values of *ca.* 370 cm^{-1}, calculated for the Racah parameter B from the spectra, are completely unacceptable. The B values for NiO_6 or NiN_6 chromophores are generally 800–900 cm^{-1} and we are not aware of any B values below *ca.* 600 cm^{-1} for six-coordinate nickel(II) (see Table IV) [11, 12].

In contrast, the spectrum of $[Ni(sal)(CH_3O)(C_2H_5OH)]_4$ is typical of regular octahedral NiO_6 systems, using the criteria discussed above, and the spectrum of $[Ni(acac)(CH_3O)(CH_3OH)]_4$ is similar, although the ν_c transition for the latter complex occurs as a very weak shoulder.

As shown above, the three bands of [Ni(eiL)-ROH]$_4$ complexes cannot be successfully assigned to ν_1, ν_2 and ν_3 of octahedral nickel(II). The only reasonable alternative is to assume that the structural distortion in the complexes lowers the symmetry of the NiO_5N chromophore sufficiently to cause splitting of the transitions of octahedral nickel(II). The ν_a and ν_b bands in the complex are therefore assigned as the split components of the ν_1 transition of six-coordinate nickel(II) (*i.e.* to the transitions $^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3B_{2g}$ in D_{4h} symmetry) [11, 13].

This assignment indicates a remarkably distorted electronic environment for the nickel(II) ion in the [Ni(eiL)ROH]$_4$ complexes. The splittings of ν_1 (4,000–4,400 cm^{-1}) may be compared with those in *trans*-NIN_4X_2 systems such as $[Ni(py)_4Cl_2]$ (2,700 cm^{-1}), $Ni(py)_4Br_2$ (3,100 cm^{-1}), $Ni(en)_2(NO_3)_2$ (5,400 cm^{-1}) and Ni(tet *a*)$(NO_3)_2$ (7,600 cm^{-1}) [11, 13, 14]. We consider that the distorted electronic environment, in the [Ni(eiL)ROH]$_4$ complexes, is caused predominantly by the structural distortion, rather than by the relative ligand field strengths of the O and N-donors in the O_5N grouping. We have no geometrically undistorted NiO_5N systems to compare with the [Ni(eiL)ROH]$_4$ complexes. However, *trans*-NiO_4N_2 systems, which should have greater tetragonal distortion caused by the relative ligand field strengths of O and N donors, produce spectra either resembling those of octahedral nickel(II) or at most indicating weak distortion, with asymmetric bands [15, 16]. This suggests that minimal distortion would occur because of the relative ligand field strengths of the donors in NiO_5N systems, therefore the very large distortion, indicated by the spectra of [Ni(eiL)-ROH]$_4$ complexes, must be caused by the structural distortion.

We are not aware of any previous reports of a structural distortion producing such a large tetragonal distortion in the electronic spectra of six-coordinate nickel(II).

Experimental Section

$[Ni(sal)(CH_3O)(C_2H_5OH)]_4$ *and* $[Ni(acac)(CH_3O)(CH_3OH)]_4$

These complexes were obtained by published methods [9, 10].

$EiaH_2$ *and* $EibaH_2$

These ligands were prepared by Jäger's method [2].

$EidbH_2$

This was prepared by refluxing dibenzoylmethane (33.6 g) and 2-aminoethanol (11 g) in dry toluene (100 ml) for 8 hr in a Soxhlet apparatus, with anhydrous aluminium oxide in the Soxhlet thimble. The solution was cooled and the resulting crystals were recrystallised from 95% ethanol to give the compound; m.p. 102–103 °C (Found: C, 76;5; H, 6.3; N, 4.9. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.2%).

$PibaH_2$

Benzoylacetone (8.1 g) and 3-amino-1-propanol (3.7 g) were refluxed in absolute ethanol (100 ml) for 3 hr. The resulting solution was cooled in an ice bath and treated with ice-cold water with vigorous stirring until the solution was turbid. After about 10 min. colourless crystals were deposited. These were filtered off, dried *in vacuo* over calcium chloride and then recrystallised from 80% methanol; m.p. 78–79 °C (Found: C, 71.4; H, 7.8; N, 6.4. $C_{13}H_{17}NO_2$ requires C, 71.2; H, 7.8; N, 6.3%). The remaining ligands were obtained as viscous liquids, which were not analysed or further purified and were used directly to prepare complexes.

$PiaH_2$

Equimolar quantities of acetylacetone (13 g) and 2-amino-1-propanol (9.7 g) were refluxed in dry toluene for 3 hr. The toluene was removed under reduced pressure on a rotary evaporator, yielding a brown viscous liquid which was used to prepare the complex.

$EietH_2$ *and* $PietH_2$

These ligands were prepared analogously to $PiaH_2$; using absolute ethanol as solvent.

$PidbH_2$

A solution of dibenzoylmethane (15.7 g) and 2-amino-1-propanol (15.7 g) in dry toluene was refluxed for 12 hr in a Soxhlet apparatus with anhydrous aluminium oxide in the Soxhlet thimble. The solvent and excess of 2-amino-1-propanol were then removed under vacuum in a rotary evaporator, yielding a viscous liquid.

β-[*Cu(eia)*]$_4$

This complex was obtained by Jäger's method [2], which has been shown by Mergehenn *et al.* to produce the β-isomer [8].

α-[*Cu(eia)*]$_4$

This was obtained by recrystallising the β-isomer from methanol, as described by Mergehenn *et al.* [8].

General Method for the Preparation of the Remaining Copper(II) Complexes

A boiling solution of copper(II) acetate hydrate (0.02 mol) in absolute methanol (150 ml) was added to a boiling solution of ligand (0.02 mol) in absolute methanol (50 ml) and the resulting mixture was boiled for 15 min and then filtered. The boiling solution was then slowly treated with a solution of sodium methoxide (0.04 mol) in absolute methanol (20 ml). The complex which precipitated was filtered off, washed with anhydrous methanol, and dried *in vacuo* over calcium chloride.

Exceptions to the above were with [Cu(eidb)]$_4$ and [Cu(pidb)]$_2$·H_2O, which precipitated upon mixing solutions of ligand and copper(II) acetate in the concentrations given above. In addition, with [Cu(eiet)]$_4$ and [Cu(piet)]$_2$, a slight excess of sodium methoxide was used.

General Method for the Preparation of Nickel(II) Complexes

Slightly impure complexes of the type Ni(eiL)-CH_3OH were obtained, as described next.

Boiling absolute methanol solutions of ligand (0.02 mol in 50 ml) and anhydrous nickel(II) acetate (0.02 mol in 200 ml) were combined and boiled for 15 min and the resulting solution was then filtered. The boiling solution was then treated with a solution of sodium methoxide (0.04 mol) in absolute methanol (25 ml) and the mixture was allowed to cool, whereupon the slightly impure [Ni(eiL)CH_3OH]$_4$ complexes deposited.

The pure complexes, [Ni(eiL)]$_2$, were obtained from the methanol adducts by the method of Bertrand and Kirkwood [3].

The pure alcohol adducts, [Ni(eiL)ROH]$_4$, were obtained by refluxing the [Ni(eiL)]$_2$ complex (*ca.* 0.0075 mol) in the appropriate alcohol (50 ml) and allowing the solutions to cool. The alcoholates were filtered off, washed with ether, and sucked dry at the pump. They were stored in an atmosphere of the appropriate alcohol. With [Ni(eia)]$_2$, all alcohols which were tried yielded adducts after refluxing the mixtures for 3 hr. With [Ni(eiba)]$_2$ and [Ni(eidb)]$_2$, refluxing for 12 hr was necessary; a wide range of alcohols was investigated but only the reported adducts could be obtained.

Analyses and Physical Measurements

Molecular weight measurements were carried out in benzene solution, using a Mechrolab 301A vapour pressure osmometer. Mass spectra were measured on an AEI MS12 spectrometer. Diffuse reflectance spectra were measured on Unicam SP500 and Zeiss PMQII spectrophotometers. Analyses and other physical measurements were as previously described [7].

References

1 R. Mergehenn and W. Haase, *Acta Cryst., B33,* 1877 (1977).
2 E. G. Jäger, *Z. Chem., 6,* 111 (1966).
3 J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta, 4,* 192 (1970).
4 J. A. Bertrand, C. Marabella and D. G. Vanderveer, *Inorg. Chim. Acta,* 26, *113 (1978).*
5 J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta, 4,* 203 (1970).
6 A. P. Ginsberg, *Inorg. Chim. Acta Rev., 5,* 45 (1971).
7 L. Merz and W. Haase, *Z. Naturforsch., 31A,* 177 (1976).
8 R. Mergehenn, L. Merz, W. Haase and R. Allmann, *Acta Cryst., B32,* 505 (1976).
9 J. E. Andrew and A. B. Blake, *J. Chem. Soc. A,* 1456 (1969).
10 J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem., 10,* 240 (1971).
11 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam (1968).
12 J. Reedijk, P. W. N. M. Van Leeuwen and W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas, 87,* 129 (1968).
13 A. B. P. Lever, *Coord. Chem. Rev., 3,* 119 (1968).
14 N. F. Curtis and Y. M. Curtis, *Inorg. Chem., 4,* 804 (1965).
15 D. P. Graddon, *Coord. Chem. Rev., 4,* 1 (1969).
16 M. Nonoyama and K. Yamasaki, *Inorg. Chim. Acta, 3,* 585 (1969).
17 M. Akbar Ali, S. E. Livingstone and D. J. Phillips, *Inorg. Chim. Acta, 6,* 552 (1972).