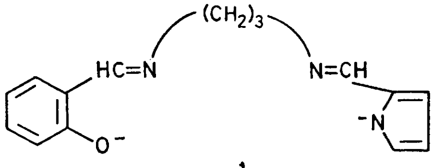
Unsymmetrical Ligand Complexes of $\mathrm{Cu^{II}}$, $\mathrm{Ni^{II}}$, and $\mathrm{Co^{II}}$ derived from Salicylaldehyde and 1,3-Propanediamine with either Pyridine-2-carbaldehyde or Pyrrole-2-carbaldehyde

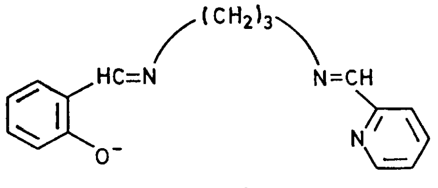
By **Philip J. Burke** and **David R. McMillin**,* Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

The 1 : 1 : 1 condensates of salicylaldehyde, propanediamine, and either pyrrole-2-carbaldehyde (L^1) or pyridine-2-carbaldehyde (L^2) have been isolated and combined with selected first-row transition-metal ions. The copper(II) and nickel(II) complexes of L^1 have been prepared and characterized, as has the pyridine adduct of the corresponding cobalt(II) derivative. The copper(II) and nickel(II) complexes of L^2 have also been characterized. Spectral and chemical properties of these systems are compared with those of complexes involving analogous symmetrical Schiff-base ligands.

THE development of routes to unsymmetrical mixed-donor (multidentate) ligands is of interest since such ligands may be useful in preparing synthetic analogues of the metal binding sites of zinc and copper proteins. Recently, Elder[1] has characterized the nickel(II) complex of the 1 : 1 condensate of salicylaldehyde with 1,3-propanediamine. We report here that upon extracting the ligand from this complex we have been able to prepare the copper(II) and nickel(II) complexes of the unsymmetrical ligands L^1 and L^2 as well as the cobalt(II) complex of ligand L^1 as the pyridine adduct.



L^1



L^2

EXPERIMENTAL

Preparation of Compounds.—Bis{*o*-[*N*-(3-aminopropyl)-formimidoyl]phenolato-*O*,*N*,*N'*}nickel(II), $[\mathrm{Ni(L^3)_2}]$, was prepared according to the published procedure.[1] Following the suggestion of Elder,[1] a solution of the ligand was obtained by refluxing $[\mathrm{Ni(L^3)_2}]$ with two equivalents of dimethylglyoxime in methanol solution for several hours and filtering out of precipitated bis(dimethylglyoximato)nickel(II).

The copper(II) and nickel(II) complexes of L^2, $[\mathrm{CuL^2}][\mathrm{NO_3}]$ and $[\mathrm{NiL^2}][\mathrm{NO_3}]$, were prepared by refluxing equimolar quantities of L^3 and pyridine-2-carbaldehyde in methanol for several hours after which time a methanol solution containing an equimolar amount of either $\mathrm{Cu[NO_3]_2{\cdot}3H_2O}$ or $\mathrm{Ni[NO_3]_2{\cdot}6H_2O}$ was added. The nickel complex precipitated immediately as fine red-brown needles. Recrystallization was achieved from methanol (Found: C, 49.75; H, 4.45; N, 14.2. Calc. for $\mathrm{C_{16}H_{16}N_4NiO_4}$: C, 49.65; H, 4.15; N, 14.5%). The copper complex was obtained as dark green crystals on standing the reaction mixture at −5 °C for 12 h (Found: C, 49.0; H, 4.25; N, 14.05. Calc. for $\mathrm{C_{16}H_{16}CuN_4O_4}$: C, 49.05; H, 4.10; N, 14.3%).

The analogous complexes of L^1, $[\mathrm{CuL^1}]$ and $[\mathrm{NiL^1}]$, were prepared in a similar manner except that two equivalents of triethylamine were added to the reaction mixture prior to the metal salt. In this case the copper(II) complex precipitated immediately as brown-green needles which were recrystallized from ethanol (Found: C, 56.55; H, 4.85; N, 13.15. Calc. for $\mathrm{C_{15}H_{15}CuN_3O}$: C, 56.85; H, 4.75; N, 13.25%). The nickel derivative was obtained as fine red needles which were recrystallized from chloroform (Found: C, 57.45; H, 5.05; N, 13.4. Calc. for $\mathrm{C_{15}H_{15}N_3NiO}$: C, 57.75; H, 4.85; N, 13.45%).

Addition of solid cobalt(II) acetate to an equimolar quantity of L^1 in dry, degassed methanol gave a yellow-orange powdered precipitate. This moisture sensitive compound, presumably $[\mathrm{CoL^1}]$, could not be obtained in a crystalline state. However, if dry, degassed pyridine was added to a suspension of the solid in refluxing methanol until all had dissolved, a red-brown semi-crystalline material, $\mathrm{CoL^1(py)}$ (py = pyridine), was obtained on cooling the solution (Found: C, 61.1; H, 5.40; N, 14.2. Calc. for $\mathrm{C_{20}H_{20}CoN_4O}$: C, 61.4; H, 5.15; N, 14.3%).

Physical Measurements.—All u.v.–visible absorption spectra were recorded at room temperature on a Cary 15 spectrophotometer. Infrared spectra were obtained from KBr pellets with a Perkin-Elmer 267 grating infrared spectrometer. Diffuse reflectance spectra were recorded on a Beckman Instruments DU-2 spectrophotometer. Electron spin resonance spectra were obtained at −180 °C on a Varian Associates E-109 spectrometer. Mass spectra were obtained on a CEC-21-110 mass spectrometer.

RESULTS AND DISCUSSION

The infrared spectra of the complexes have no bands between 3 100 and 4 000 $\mathrm{cm^{-1}}$, indicating the absence of unreacted amine, unco-ordinated OH, and water. Bands at 1 340 cm^{-1} and at 825 cm^{-1} observed in the spectra of [CuL^2][NO$_3$] and [NiL^2][NO$_3$] may be attributed to ionic nitrate.[2] The i.r. spectra of [CuL^1] and [NiL^1] are similar, though not identical, to the spectra of the corresponding symmetrical salicylaldehyde (L^4) and pyrrole (L^5) complexes. The most notable differences occur in the region of the azomethine (–HC=N–) stretching modes. The L^4 complexes exhibit a band at *ca.* 1 620 cm^{-1} whereas the L^5 complexes exhibit a band at *ca.* 1 585 cm^{-1}. Understandably, the complexes of the unsymmetrical ligands L^1 and L^2 exhibit both bands.

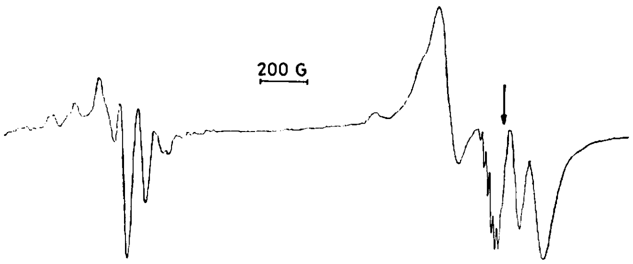
In the mass spectra of [CuL^1] and [NiL^2] intense peaks are observed at the masses of the respective molecular ions. At high *m/e* values, peaks characteristic of the respective dimers were also observed; no evidence for the presence of the symmetrical ligand analogues was apparent, however. Solid-state and solution u.v.–visible spectral data for the nickel(II) and copper(II) complexes of L^1 and L^2 (Table) are consistent with the presence of square-planar or distorted square-planar geometries [3–7] but the interpretation of the absorption spectra is complicated by the fact that the dimerization may occur in solution, see below. The solution u.v.–visible spectrum of CoL^1(py) is featureless over the range 300—700 nm and the solid spectral data do not allow an unambiguous assignment of the structure of this complex. It does not seem unreasonable, however, to expect a pyramidal structure similar to that reported for the analogous complex [CoL^6(py)][L^6 = *NN'*-ethylenebis(salicylideneiminate)].[8]

Electronic spectra

Compound	Solvent	$\lambda_{max.}$ (ε) [a]
[CuL^1]	CHCl$_3$	17.95 (137); 27.78 (16 300); 32.79 (sh); 36.76 (1 800)
[CuL^1]	Pyridine	16.72 (125); 28.25 (17 600)
[NiL^1]	CHCl$_3$	18.52 (sh); 25.00 (sh); 27.10 (1 300); 31.15 (9 900)
[CuL^2][NO$_3$]	H$_2$O	17.27 (64); 28.33 (4 300); 33.67 (sh); 34.84 (sh); 37.31 (16 750)
[NiL^2][NO$_3$]	H$_2$O	28.33 (4 830); 36.50 (11 400)
[CuL^4] [b]	CHCl$_3$	16.58 (240)
[NiL^4] [b]	CHCl$_3$	16.80 (sh)
[CuL^5] [c]	CHCl$_3$	18.00 (113); 28.09 (16 300); 33.22 (10 900); 34.97 (16 100)
[NiL^5] [d]	CHCl$_3$	23.87 (sh); 25.25 (9 400); 26.31 (sh); 31.44 (2 700)
[CuL^1]		15.38 (sh); 17.86; 26.32
[NiL^1]		18.87 (sh); 26.32 (sh)
[CuL^2][NO$_3$]		15.62 (sh); 18.18; 26.32 (sh)
[NiL^2][NO$_3$]		16.95 (sh); 20.83 (sh); 21.74
CoL^1(py)		12.66; 19.23 (sh); 25.01

[a] Units are 10^{-3} cm^{-1} (dm^3 mol^{-1} cm^{-1}); sh = shoulder. [b] Ref. 7. [c] H. C. Clark and A. L. O'Dell, *J. Chem. Soc.*, 1956, 520. [d] Ref. 5.

Electron spin resonance spectra of the copper(II) derivatives of L^1 have been obtained in frozen solutions. In frozen xylene solution at −180 °C the e.s.r. spectrum of [CuL^1] is well resolved showing signals from both $\Delta M_s = 1$ and $\Delta M_2 = 2$ transitions (Figure). The signals closely resemble those reported[9] for [CuL^4] in frozen xylene solution and are consistent with the presence of dimeric species in solution. The structure of each dimeric unit is probably similar to the solid-state structure of [CuL^6] [10] in which each copper atom achieves five-co-ordination *via* bridging phenolic oxygens. A feature observed in the frozen xylene spectrum of [CuL^1], but apparently not in that of [CuL^4], is the presence of nitrogen hyperfine splitting (*ca.* 15 G *) in addition to that of copper. Splitting by two equivalent and one non-equivalent nitrogen atoms should give rise to a 15-line hyperfine pattern, but only eight lines are clearly resolved, presumably all attributable to splitting from the nitrogens. A dimeric structure is also likely for [NiL^1]; on the basis of crystallographic data it has been proposed[11] that the solid-state structure of [NiL^6] is similar to that of [CuL^6].



The e.s.r. spectrum of [CuL^1] in xylene at −180 °C. The microwave frequency was 9.089 GHz. The high-field portion was run at a power of 10 mW and a gain setting of 4 × 10^3 while the low-field region was run at 40 mW with a gain of 2.5 × 10^4. The marker indicates the field for $g = 2$

In frozen CHCl$_3$ solution at −180 °C the e.s.r. spectrum of [CuL^1] is that expected for a mixture of monomeric and dimeric species.† The differing species distributions probably arise because CHCl$_3$ is weakly hydrogen-bonding whereas xylene is weakly basic. It can also be noted that CHCl$_3$ forms a 1 : 1 adduct with [CuL^6].[10,12,13] In frozen pyridine solution an apparently axial e.s.r. spectrum was obtained for [CuL^1] ($g_{\parallel} = 2.210$, $A_{\parallel} = 0.018\ 1$ cm^{-1}), reflecting the more effective competition of solvent pyridine for co-ordination sites around the Cu^{II} ions. Half-field transitions were not detected in the frozen pyridine solution nor in the spectrum of powdered [CuL^1]. The compound [CuL^2][NO$_3$] was found to be insufficiently soluble in non-polar solvents for e.s.r. measurements precluding the investigation of possible dimer formation. In any case the relatively close approach of two monomer units {2.4 Å for [CuL^6] [10]} is likely to be less favourable for the cationic complexes. No e.s.r. signal was observed for CoL^1(py) in either frozen pyridine or frozen chloroform at −180 °C.

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* Throughout this paper: 1 G = 10^{-4} T.

† The spectrum is comparable to that previously reported (ref. 13) for [CuL^4] in frozen CHCl$_3$ solution.

REFERENCES

[1] R. C. Elder, *Austral. J. Chem.*, 1978, **31**, 35.

[2] B. M. Gatehouse, J. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1957, 4222.

[3] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.

[4] K. S. Patel and J. C. Bailar, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1399.

[5] J. H. Weber, *Inorg. Chem.*, 1967, **6**, 258.

[6] R. E. Clarke and J. H. Weber, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1937.

[7] R. H. Holm, *J. Amer. Chem. Soc.*, 1960, **82**, 5632.

[8] N. Caligares, D. Minichelli, G. Nardin, and L. Rondaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[9] D. J. Cookson, T. D. Smith, and J. R. Pilbrow, *Bull. Chem. Soc. Japan*, 1975, **48**, 2832.

[10] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.

[11] H. Montgomery and B. Morosin, *Acta Cryst.*, 1961, **14**, 551.

[12] A. C. Braithwaite, C. E. F. Rickard, and T. N. Waters, *J.C.S. Dalton*, 1975, 2149.

[13] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.