

Complexes of Quadri- and Quinquidentate, Mono- and Bis-Schiff-Base Ligands Derived from Acetylpyridine

R. H. PRINCE and D. A. STOTTER

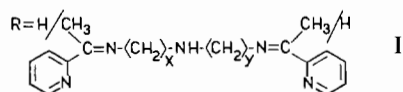
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Received January 17, 1974

The preparation is reported of a series of metal(II) complexes of a quinquidentate ligand produced *in situ* or by complexation with the Schiff-base condensation-product of two moles of 2-acetylpyridine with 3,3'-iminobispropylamine. From the *in situ* synthesis of the Ni(II) compound only a quadridentate, mono-Schiff-base complex with coordinated acetyl-pyridine is isolable. The effect of varying the triamine used in this preparation is described and rationalised by consideration of ligand-strain, the effect of stability-constants on ligand-dissociation, and the influence of the acetyl- (as opposed to a formyl-) group. Analytical data, infra-red studies, magnetic moments and solution-spectra of the complexes are described, and the inter-conversion of the two types of Ni(II) complex investigated.

Introduction

Quinquidentate ligands have been the subject of few studies, possible structural types have, however, been excellently reviewed.¹ Complexes of ligands of this kind derived from Schiff-base condensation of triamines with salicylaldehydes have been investigated,^{2,3} and Spencer and Taylor have prepared Ni(II) and Co(II) complexes of pre-formed ligand I (R = H,

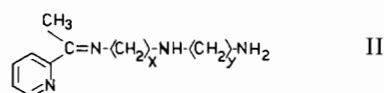


$x = y = 3$) presenting evidence for its quinquidentate behaviour.^{4,5} A complex of this ligand wherein the two Schiff-base linkages have been hydrogenated has also been reported, but apparently not further investigated.⁶ The effect of metal ions on Schiff-base ligand formation has been reviewed by Lindoy.⁷

For use in several studies⁸ we have produced a series of metal complexes of ligand I (R = CH₃) using an *in situ* method.⁷ It is found that the complexation of Ni(II) varies with the mode of preparation and with the nature of the triamine employed.

Hereafter we shall refer to ligand I (R = CH₃) as L_{xy} to specify the triamine used in its preparation;

similarly ligand II, in which only one imine-linkage has formed, will be referred to as M_{xy}.



Preparation

The complexes were prepared *in situ* by gently refluxing two equivalents of 2-acetylpyridine (AcPy) plus one equivalent of the triamine 3,3'-iminobispropylamine with one equivalent of a salt of the required metal, with a poorly-coordinating anion, in aqueous ethanol for 6 hours. Addition of the triamine raises the pH and metal hydroxide may precipitate; this is overcome by adding a few drops of acetic acid. The ethanol was evaporated and aqueous sodium perchlorate added to bring down the complexes in high yields as the bis-perchlorate salts. Recrystallisation from water produced crystals, the analyses of which are presented in Table I. The Mn(II) complex could not, however, be prepared *in situ* since brown MnO₂ was rapidly deposited even under nitrogen (always, of course, necessary for the Co(II) species). The free ligand was thus produced by heating a 2:1 mole-ratio of AcPy and the triamine in ethanol for some hours in the presence of molecular sieve to remove water. The orange solution was allowed to stand and addition of Mn(II) gave the required complex; this was recrystallised from acetonitrile-diethylether since rapid hydrolysis takes place in hot water.

Using the *pre-formed* ligand a different Ni(II) complex to that obtained from the *in situ* synthesis was isolated, though the Co(II) and Cu(II) complexes formed in the two preparations were the same. To investigate the effect of varying the triamine, the Ni(II) *in situ* preparation was repeated using diethylenetriamine, ($x = y = 2$), N-(2-aminoethyl)-1,3-propanediamine ($x = 2, y = 3$), spermidine ($x = 3, y = 4$), and the analogue of 3,3'-iminobispropylamine in which the secondary amino group is methylated. The analyses of the resultant complexes are given in Table I; the

TABLE I. Microanalytical Data.^a

Compound	% Required			% Found		
	C	H	N	C	H	N
Mn·L ₃₃ ·(ClO ₄) ₂	40.9	4.8	12.1	40.6	4.6	11.8
Co·L ₃₃ ·(ClO ₄) ₂	40.3	4.6	11.7	40.1	4.6	11.7
Ni·L ₃₃ ·(ClO ₄) ₂ ·H ₂ O	39.2	4.8	11.4	39.4	4.8	11.5
Ni·M ₃₃ ·AcPy·(ClO ₄) ₂	39.2	4.8	11.4	39.0	4.7	11.2
Ni·M ₂₂ ·AcPy·(ClO ₄) ₂	36.9	4.3	12.0	37.1	4.3	12.1
Ni·M ₃₂ ·AcPy·(ClO ₄) ₂	38.1	4.6	11.7	38.1	4.4	11.5
Ni·L ₃₄ ·(ClO ₄) ₂ ·H ₂ O	40.2	5.0	11.2	40.1	4.9	11.3
Ni·L _{Me} ·(ClO ₄) ₂ ·H ₂ O	40.2	5.0	11.2	40.4	4.8	11.2
Cu·L ₃₃ ·(ClO ₄) ₂	40.0	4.5	11.7	40.2	4.6	11.6
Zn·L ₃₃ ·(ClO ₄) ₂ ·H ₂ O	38.7	4.7	11.3	38.8	4.4	11.4
Cd·L ₃₃ ·(ClO ₄) ₂	37.0	4.2	10.8	37.1	4.1	10.3
Cd·M ₃₃ ·Cl·ClO ₄	32.4	4.6	11.6	32.5	4.4	11.3

^a All analyses performed by Mr. D. Flory at these laboratories.

formulations implied are supported by the infra-red spectra of the complexes described below.

The use of CdSO₄ in the *in situ* synthesis gave only the bis-imino product, but using CdCl₂ the only compound isolable was that in which only one imino-linkage had formed (Table I); this was obtained in good yield. With ZnBr₂ a similar effect was observed. In this case the bis-imino compound has been obtained pure from mixtures by fractional crystallisation from water in which the mono-imino species is more soluble.

Infra-Red Spectra

That a water molecule is present in the Zn complex and in the Ni complexes prepared from pre-formed L₃₃ and *in situ* L₃₄ and L_{Me}, and is absent in the compounds of Mn, Co, Cu and Cd is confirmed by the presence or otherwise of a broad band around 3500 cm⁻¹. In the case of the Ni complexes of M₂₂, M₂₃

and M₃₃ however, no such band is apparent; instead strong sharp bands are present in the N-H stretching region below 3400 cm⁻¹ in addition to those observed for the other metal complexes (Table II).

In all cases the C=C and C=N absorptions of the pyridine rings are respectively at 1574 ± 1 cm⁻¹ and 1600 ± 2 cm⁻¹, and a broad and intense ClO₄ absorption is present around 1100 cm⁻¹. In the spectra of complexes of ligands L the imine stretches occur as a pair of bands exhibiting solid-state splitting; the assignment of these band has been discussed elsewhere.⁹ Spencer and Taylor observe bands between 1635 and 1648 cm⁻¹ for the Ni complexes of ligand I (R = H),⁴ and a band at 1630 cm⁻¹ for the analogous Co(II) complex;⁵ in neither case were spectra like those of the complexes of ligands M observed.

The strength and position of the major absorption in the C=O/C=N stretching region for Ni complexes of M₂₂, M₃₂ and M₃₃ leads us to assign it to a coordi-

TABLE II. Infra-Red Data.^a

Complex (ClO ₄ salt)	O-H/N-H Stretching Region, cm ⁻¹	Exocyclic C = N Stretch, cm ⁻¹
Mn·L ₃₃	3242	1647 1628
Co·L ₃₃	3220 3165(b)	1627
Ni·L ₃₃ ·H ₂ O	3500(vb) 3256	1640 1631
Ni·M ₃₃ ·AcPy	3321 3281 3262(s) 3186(sh)	1666(vs) ^b 1659(sh) 1623
Ni·M ₂₂ ·AcPy	3343 3295(s)	1660 ^b (vs, b)
Ni·M ₃₂ ·AcPy	3350(sh) 3331 3281(s)	1659(vs) ^b 1625
Ni·L ₃₄ ·H ₂ O	3500(vb) 3260	1641 1626
Ni·L _{Me} ·H ₂ O	3500(vb)	1641 1629
Cu·L ₃₃	3227 3200(b)	1644 1640(sh) 1631
Zn·L ₃₃ ·H ₂ O	3500(vb) 3235 3189(b)	1659 1654(sh) 1645
Cd·L ₃₃	3246	1654 1657(sh) 1637
Cd·M ₃₃ ·Cl	3225 3285 3330(s)	1640

^a Recorded in Nujol on a Perkin-Elmer 257 instrument using a polystyrene film calibrant; b: broad, s: strong, sh: shoulder. ^b C = O stretch; see text.

nated C=O vibration of acetylpyridine. Complexes of 2-acetylpyridine alone have been investigated by Kirson^{10,11} who has demonstrated coordination in both the keto and enol forms; the ketonic Ni(II) complexes Ni(AcPy)₂(halide)₂ exhibit strong C=O bands at 1665–1670 cm⁻¹, while enolic complexes have C=C bands around 1600 cm⁻¹. In the reaction of ethylenediamine with acetone Curtis has reported an intermediate Ni(II) complex wherein acetone-like C=O bonds absorb at 1690 and 1682 cm⁻¹¹² – the drop in frequency on coordination being comparable to that observed here (C=O stretch in AcPy 1701 cm⁻¹, in acetone 1710 cm⁻¹). In a similar Cu(II) complex wherein one imine bond has formed, the C=N stretch is at 1667 cm⁻¹, and a C=O stretch at 1692 cm⁻¹.¹²

The additional strong bands in the N–H stretching region we assign to the primary amino N–H stretches of ligands M. This is confirmed by the resemblance of this region of their spectra to that of the Cd·M₃₃ complex (Table II). When the Ni complexes of ligands M were recrystallised from D₂O, additional bands in the ‘fingerprint’ region shifted to extents compatible with N–H/N–D bending and C–NH/C–ND stretching modes,¹³ and the N–H stretching bands moved to lower frequencies such that $\nu_D/\nu_H \sim .73$ in good agreement with the simple harmonic oscillator model.¹³

Preliminary results of a single-crystal X-ray structural determination on the Ni·M₃₃·AcPy·(ClO₄)₂ compound¹⁴ fully support the above structural conclusions.

Magnetic Measurements

The results of room-temperature magnetic-moment determinations by the standard Gouy method on finely powdered samples at 23°C are given in Table III; Pascal corrections for ligand and inner-core diamagnetism have been applied.

The analogous Co(II) complex of ligand I (R = H) has a moment of 1.91 B.M.,⁵ while the Ni(II) complex of this quinquidentate ligand has a moment of 3.31 B.M.⁴ The value for the Cu complex (Table III) shows it to be magnetically dilute. The values for the Ni(II) compounds confirm that they are high-spin, but magnetic data alone is insufficient for an assignment of

octahedral stereochemistry.¹⁵ This is, however, implied by the visible-spectra of the complexes, and is confirmed in the case of the Ni·M₃₃·AcPy·(ClO₄)₂ compound by the X-ray structure.¹⁴

Electronic Spectra

These were recorded in acetonitrile; qualitatively similar spectra were obtained in water but solubility difficulties were encountered. The white Zn complex shows only absorption bands due to the ligand at 238 nm ($\epsilon = 1.56 \times 10^4$), 280 nm (1.58×10^4) and 286 nm (1.36×10^4 , sh). These absorptions are as expected for imino-substituted pyridine rings.¹⁶ The blue Cu compound displays a broad absorption at 636 nm ($\epsilon = 200$), with less well-defined bands around 800 nm and 400 nm ($\epsilon \sim 150$); the compound is obtained free from coordinated acetonitrile on addition of ether to the solution. A diffuse reflectance spectrum shows a broad band centred at 616 nm (16.2 kK); it has been suggested that this would indicate square-pyramidal stereochemistry,¹⁷ but this approach has been questioned.¹⁸ For the Ni complexes the absorbance values are so low that only humps are apparent on the strong ligand absorption tailing into the visible. The ligand-absorption in the ultra-violet is very similar for Ni·L₃₃ and Ni·M₃₃·AcPy indicating the same degree of unsaturation; in the case of the latter compound the peaks in the visible occur at 525 nm ($\epsilon = 6$) and 560 nm, (7), with another peak at longer wavelength indicated by a rising absorption towards 850 nm. Very similar spectra to this are obtained for all the Ni complexes herein described, and indicate an octahedral stereochemistry in solution;¹⁵ they are obtained free from acetonitrile on addition of ether to the solution. The Mn complex exhibits two broad, poorly-defined bands at 350 and 430 nm (ϵ 50–100) and is pale-orange. The Co complex is brown with a charge-transfer band ($\epsilon = 1.6 \times 10^3$) at 435 nm.

Discussion

The above results show that an *in situ* preparation of complexes of ligand L₃₃ with Co(II), Cu(II), Zn(II) and Cd(II) is successful, whereas with Ni(II) it is not – only one Schiff-base linkage forming to produce ligand M₃₃ and a molecule of acetylpyridine coordinating to form an octahedral structure. As the degree of strain – as shown by molecular models – in the potential ligand L is increased by the use of triamines with shorter methylene chains, the same type of complexes are isolated – those of M₃₂ and M₂₂. However, when the potential ligand L is elongated, or the ‘bite’ at the secondary nitrogen slightly increased by the use of N-methylated triamine, complexes of L₃₄ and L_{Me}

TABLE III. Magnetic Data.

Compound	$\chi_M^{\text{corr}} \times 10^{-3}$ c.g.s. units	$\mu_{\text{B.M.}}$
Co·L ₃₃ ·(ClO ₄) ₂	1.51	1.89
Cu·L ₃₃ ·(ClO ₄) ₂	1.58	1.98
Ni·M ₃₃ ·AcPy·(ClO ₄) ₂	4.57	3.29
Ni·M ₂₂ ·AcPy·(ClO ₄) ₂	4.24	3.18
Ni·M ₃₂ ·AcPy·(ClO ₄) ₂	4.15	3.14
Ni·L ₃₄ ·(ClO ₄) ₂ ·H ₂ O	4.68	3.33

are isolated. When L_{33} is pre-formed, it will coordinate to Ni unchanged.

The interconversion of the $Ni \cdot L_{33}$ and $Ni \cdot M_{33} \cdot AcPy$ complexes was investigated by refluxing these compounds separately in water, under various conditions of pH, and in methanol. In all cases the complexes crystallised unchanged, as shown by their infra-red spectra. Only in the presence of a large excess of AcPy could the $Ni \cdot M_{33} \cdot AcPy$ complex be converted to the $Ni \cdot L_{33}$ species. Since the reaction could only be followed via the isolation of crystals, little can be deduced about the equilibria present in solution (this point is discussed in ref. 19), but it is apparent from the above that there exists a high kinetic barrier to the interconversion.

The stability of the $Ni \cdot L_{33}$ species to hydrolysis has many parallels among known Schiff-base complexes,⁷ but the stability of the $Ni \cdot M_{33} \cdot AcPy$ compound was unexpected. It may be rationalised as follows. For the compound to react further intramolecularly to produce the $Ni \cdot L_3$ species, the coordinated primary amino-group must dissociate and nucleophilically attack the coordinated carbonyl-carbon. This is not a fast process because the dissociative step takes the Ni from a 6 to a 5-coordinate species, this being accompanied by a crystal-field destabilisation²⁰ which, despite the crudeness of the theoretical model, may be quite large. This is reflected in the relatively slow rates of substitution found for 'labile' Ni(II) complexes,²¹ and may explain why the formation of ligands M was only observed (in the presence of poorly-coordinating anions) in the case of Ni. In addition, the methyl-group on the carbonyl-carbon is producing an inductive and steric barrier to nucleophilic attack.

We have observed that an *in situ* preparation of the Ni complex of ligand I ($R = H, x = y = 3$) goes to completion very quickly, producing a compound identical to that made from the pre-formed ligand by addition of Ni(II).⁴ This indicates that the methyl-group of the acetyl-moiety is the most important contributor to the kinetic barrier discussed above. It is noticeable in the literature that most workers employ formyl-groups to produce the Schiff-base type of linkage; it is probably only for this reason that more examples of the kind of complex described herein have not been observed.

The *in situ* synthesis of $Ni \cdot L_{34}$ and $Ni \cdot L_{Me}$ is probably successful because, as we have found with the corresponding triamines,²² the stability constants of M_{34} and M_{Me} with Ni and other metals will be lower than that of M_{33} . In the former case this is due to the presence of a seven-membered chelate-ring, in the latter due to the low basicity of the tertiary nitrogen.²³ Thus in these two compounds the primary amino-group will be more likely to become free, and when free will be more able to attack the carbonyl-carbon because of the longer methylene chain or the increased N-'bite'.

That a large excess of AcPy will produce $Ni \cdot L_{33}$ from $Ni \cdot M_{33}$ may be explained by the dissociated amino-group being able to attack a free carbonyl-carbon which is close rather than a coordinated one which, at least in the solid-state,¹⁴ is comparatively distant. Excess AcPy will also convert $Cd \cdot M_{33}$ to $Cd \cdot L_{33}$; the initial formation of the former is due to displacement of AcPy from the Cd by chloride ion, which not only deactivates the AcPy but removes it from the sphere of efficient attack by the amino-group until an excess of AcPy is present. That this is a kinetic effect is shown by the production of $Cd \cdot L_{33}$ from the original reaction-mixture on long-standing.

Acknowledgement

D.A.S. thanks the Science Research Council for a grant.

References

- 1 F. Lions, *Rev. Pure Appl. Chem.*, **19**, 177 (1969).
- 2 W.M. Coleman and L.T. Taylor, *Inorg. Chem.*, **10**, 2195 (1971).
- 3 L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).
- 4 C.T. Spencer and L.T. Taylor, *Inorg. Chem.*, **10**, 2407 (1971).
- 5 C.T. Spencer and L.T. Taylor, *ibid.*, **12**, 644 (1973).
- 6 H.A. Goodwin in 'Chelating Agents and Metal Chelates' (Ed. F.P. Dwyer and D.P. Mellor), p. 168, Academic Press, 1964.
- 7 L.F. Lindoy, *Quart. Rev. Chem. Soc.*, **25**, 379 (1971).
- 8 P.R. Woolley, Ph.D. Thesis, University of Cambridge, 1973. R.H. Prince and D.A. Stotter, Unpublished work.
- 9 D.H. Busch and J.C. Bailor, *J. Am. Chem. Soc.*, **78**, 1137 (1956).
- 10 B. Kirson, *Israel J. Chem.*, **6**, 1 (1968).
- 11 B. Kirson, *ibid.*, **8**, 709 (1970).
- 12 N.F. Curtis, *J. Chem. Soc. Dalton*, 1357 (1972).
- 13 S. Pinchas and I. Laulicht, 'Infra-Red Spectra of Labelled Compounds', Academic Press, 1971.
- 14 G.M. Sheldrick and D.A. Stotter, Forthcoming publication.
- 15 L. Sacconi, *Transition Metal Chem.* (Ed. R.L. Carlin), **4**, 199 (1968).
- 16 D.H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry', McGraw-Hill, 1966.
- 17 B.J. Hathaway, *J. Chem. Soc. Dalton*, 1196 (1972).
- 18 E.D. McKenzie, *J. Chem. Soc. A*, 3095 (1970).
- 19 M. Cressey, E.D. McKenzie and S. Yates, *J. Chem. Soc. A*, 2677 (1971).
- 20 D. Benson, 'Mechanisms of Inorganic Reactions in Solution', McGraw-Hill, 1968.
- 21 R.G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
- 22 R.H. Prince, D.A. Stotter and P.R. Woolley, *Inorg. Chim. Acta*, **9**, 51 (1974).
- 23 D.A. Goldberg and W.C. Fernelius, *J. Phys. Chem.*, **63**, 1328 (1959).