Inorganica Chimica Acta, *93* (1984) L43–L45

The Synthesis and Characterization of the Macrocyclic and Ring-opened Complexes Formed in the Reaction of Nickel(II) and Cobalt(II) Ions with 2,6-Diacetylpyridine and Hydrazine*

WANDA RADECKA-PARYZEK

Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland

Received May 12, 1984

The intense interest in synthetic macrocycles and their metal complexes depends on the fact that they mimic naturally occurring macrocyclic molecules in their structural and functional features, and in their rich chemical behavior. Of these, macrocyclic complexes with four nitrogen donor atoms have attracted considerable attention. Most macrocyclic ligands are best prepared with the aid of metal ions as templates to direct the steric course of the condensation reactions, which ultimately end with ring closure [1].

In previous papers we have described the template synthesis and characterization of Mg(II), Zn(II) [2] and Sc(III) [3] 14-membered polyaza macrocyclic complexes and the preparation and properties of the macrocyclic and ring-opened complexes of lanthanides formed in the reaction of metal ions with 2,6-diacetylpyridine and appropriate amines [4–6].

As a continuation of our studies on the effect of the nature and size of both the metal and the macrocycle on the structure of the complex formed, and on the effectiveness of different metal ions in promoting macrocycle synthesis, we now report the template action of Ni(II) and Co(II) ions in the synthesis of a planar quadridentate hexaaza macrocycle.

The macrocyclic complexes of stoichiometry $[NiL^1(H_2O)_2](ClO_4)_2\cdot 4H_2O$ and $[CoL^1(H_2O)_2](ClO_4)_2\cdot 4H_2O$, where L^1 is 2,5,11,14-tetramethyl-3,4,12,13,19,20-hexaazatricyclo[13.3.1.$1^{6,10}$] eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene, were prepared by the reaction of 2,6-diacetylpyridine (2 mmol) with hydrazine (2 mmol) in the presence of metal perchlorates (4 mmol) in refluxing ethanol with yields of 83% and 89%, respectively. The formulations of these complexes follow from spectral data (i.r., uv–vis, e.s.r.) and thermal analysis. Elemental analysis figures are consistent with the above formulae (calc. for Ni complex: C, 31.60; H, 4.42; N, 12.29%; found: C, 31.51; H, 4.36; N, 12.37%; calc. for Co complex: C, 31.59; H, 4.42; N, 12.28%; found: C, 31.68; H, 4.48; N, 12.18%). The complexes appear to be air stable solids, moderately soluble in acetonitrile.

The infrared spectra of these complexes (in KBr pellets, 4000–400 cm^{-1}) confirm the formation of the macrocyclic compounds by the absence of uncondensed functional group stretching modes of starting materials and the appearance of a strong absorption band at *ca.* 1600 cm^{-1} attributable to the coordinated C=N stretching mode [5, 7]. The high and low energy pyridine bands are observed at *ca.* 1570, 1460, 635 and 420 cm^{-1} suggesting coordination of pyridine [2–6, 8]. The presence of non-coordinated perchlorates in the complexes is inferred from the broad, intense band centered at 1100 cm^{-1} and a strong sharp band at 625 cm^{-1}, and also from the absence of splitting of the degenerate stretching and bending modes of the ClO_4^- ion, which is indicative of coordination species [9]. A broad diffuse band in the 3500–3200 cm^{-1} region is assigned to O–H stretching modes for lattice water. A weak absorption observed at 530 cm^{-1} suggests that coordinated water is also present [2–6, 10].

The electronic spectra of acetonitrile solutions of the complexes exhibit bands at *ca.* 270 and 335 nm attributable to the $\pi \rightarrow \pi^*$ transitions of coordinated macrocycle.

The electron spin resonance spectra of the cobalt(II) complex taken in solution and in the solid state at room and liquid nitrogen temperatures give a value of $g = 2.2$ characteristic of spin paired complexes of Co(II) with square planar or octahedral symmetry [11].

Further evidence for the formation of the macrocycle comes from the mass spectra of the complexes. The highest m/z fragment observed at m/z 318 corresponds to the molecular weight of the uncoordinated macrocycle. The occurrence of a strong peak corresponding to the free macrocycle instead of the parent ion peak of the macrocyclic complexes is quite common for the other polyaza macrocycles and has been reported in the mass spectra of these compounds [6, 12].

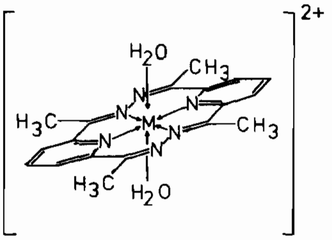
The thermogravimetric analysis indicates for these two complexes a loss of four molecules of water at 30–60 °C, and two water molecules at 120–160 °C.

On the basis of spectral and analytical data, along with the molecular model analysis, it seems reasonable to assume that these complexes have a six coordinate tetragonally distorted octahedral structure (I) with the macrocycle occupying the equatorial plane and the axial positions being filled with water. This structure is highly stabilized by the formation of two five- and two six-membered chelate rings upon

---

*Presented in part at the First International Conference on Bioinorganic Chemistry, Florence, Italy, June 13–17, 1983.

0020-1693/84/$3.00



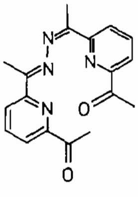
I

coordination, which allows the high resonance of the system. The complexes satisfy the Hückel criterion having 14π electrons in the inner ring and are therefore chemically stable and comparable in this regard with the derivatives of phthalocyanines and porphyrins.

The synthesis of the free ligand has also been achieved in two stages under high dilution conditions without the use of the coordination template effect, albeit with very low yield [2]. The importance of the metal ion in promoting the cyclic condensation of the reactants instead of the competing linear polymerization reaction is thus apparent.

In addition to the ring closed complexes discussed above, the ring-opened (6-acetyl-pyrid-2-yl) methyl ketone azine (L^2) complexes of Ni(II) and Co(II) ions were isolated from reaction of 2,6-diacetylpyridine with hydrazine in the presence of metal perchlorates and identified by spectra data and thermal analysis. Chemical analysis established the stoichiometries of the complexes isolated to be $[NiL^2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (calc.: C, 31;42; H, 4.39; N, 8.14%; found: C, 31.36; H, 4.46; N, 8.22%) and $[CoL^2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (calc.: C, 31.41; H, 4.39; N, 8.14%; found: C, 31.34; H, 4.36; N, 8.17%). These complexes appear to be identical with those prepared in the direct synthesis in which the appropriate metal perchlorate reacts with (6-acetyl-pyrid-2-yl)methyl ketone azine in refluxing ethanol for 4 hours.

It should be noted here that free (6-acetyl-pyrid-2-yl) methyl ketone azine (**II**) is an intermediate in the preparative route to the free L^1 macrocycle and was isolated and characterized in the manner described earlier [2].



II

The infrared spectra of these two complexes are very similar and are analysed in comparison with that of the free ligand. The most diagnostic band is the C=N stretching mode indicating the partial condensation reaction. This band, observed in the spectrum of the ligand at 1600 cm^{-1}, is shifted to lower frequencies by 40 cm^{-1} upon complex formation suggesting that the double bond character of C=N decreased as a consequence of coordination by the nitrogen atom [5, 13]. An important feature common to Ni(II) and Co(II) L^2 complexes is the occurrence of two medium absorption bands at 1700 and 1650 cm^{-1} assigned to C=O stretching modes. In the infrared spectrum of the free ligand this absorption appears at 1695 cm^{-1}. The shift of this band to lower frequency in the complexes clearly indicates coordination through the oxygen atom [5, 14].

The position of the other νC=O band at a slightly higher frequency than in the free ligand suggests that one of the two carbonyl groups remains uncoordinated [5, 15]. Bonding of the pyridine ring is shown by an increase in the frequency of the higher and lower energy pyridine ring vibrations by about 15–40 cm^{-1} in the complexes relative to the ligand. Such changes indicate the coordination of pyridine nitrogen [5]. The infrared spectra of these two complexes show a very strong band at around 1100 cm^{-1} and another band at 625 cm^{-1}, neither of which has undergone any splitting, indicating the presence of ionic perchlorate. The νOH band appears as a broad absorption at 3420 cm^{-1}. A weak absorption is found at 870 and 550 cm^{-1} as expected for coordinated water. The presence of water bound in two different ways is supported by the results of thermogravimetric analysis. The complexes indicate the loss of four water molecules at 50–70 °C and two molecules of water at 130–160 °C.

The electronic spectra of Ni(II) and Co(II) complexes of (6-acetyl-pyrid-2-yl)methyl ketone azine for solutions in acetonitrile consist of three bands at *ca.* 245, 265 and 310 nm. The free ligand exhibits two bands at 232 and 288 nm. The differences in the spectra can be attributed to changes in energy levels of the ligand orbitals in coordination [13].

Parent ion peaks were not observed in the mass spectra of the complexes which showed instead a highest peak at m/z 322 corresponding to the free ligand.

On the basis of available evidence a tentative coordination number of six can be assigned in these complexes, which is achieved by coordination through the oxygen atom of one of the two carbonyl groups and three nitrogen donor atoms of the ligand with sufficient axial interaction of two water molecules to produce a distorted octahedral symmetry.

References

1 D. H. Busch, *Rec. Chem. Prog.*, *25*, 107 (1964);
L. F. Lindoy and D. H. Busch, in W. Jolly (ed.), 'Preparative Inorganic Reactions, Vol. 6', Interscience, New York, 1971, p. 1–61;

N. F. Curtis, *Coord. Chem. Rev., 3,* 3 (1968);
L. F. Lindoy, *Chem. Soc. Rev., 14,* 421 (1975);
J. J. Christensen, D. J. Eatough and R. M. Izatt, *Chem. Rev., 74,* 351 (1974);
G. Newkome, J. D. Sauer, J. M. Roper and D. C. Hager, *Chem. Rev., 77,* 513 (1977);
D. H. Busch, *Inorg. Synth., 18,* 2 (1978);
G. A. Melson, 'Coordination Chemistry of Macrocyclic Compounds', Plenum, New York, 1979.

2 W. Radecka-Paryzek, *Inorg. Chim. Acta, 34,* 5 (1979).

3 W. Radecka-Paryzek, *Inorg. Chim. Acta, 35,* L349 (1979).

4 W. Radecka-Paryzek, *Inorg. Chim. Acta, 45,* L147 (1980).

5 W. Radecka-Paryzek, *Inorg. Chim. Acta, 52,* 261 (1981).

6 W. Radecka-Paryzek, *Inorg. Chim. Acta, 54,* L251 (1981).

7 S.-M. Peng, G. G. Gordon and V. L. Goedken, *Inorg. Chem., 17,* 119 (1978).

8 N. S. Gill, R. H. Nuttall and D. E. Scaife, *J. Inorg. Nucl. Chem., 18,* 79 (1961).

9 B. J. Hathaway and E. Underhill, *J. Chem. Soc.,* 3091 (1961).

10 M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy and S. M. Nelson, *J. Chem. Soc., Dalton Trans.,* 438 (1977).

11 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.,* 338 (1959);
A. Zalewsky and H. Ferz, *Helv. Chim. Acta, 56,* 977 (1973);
K. Farmery, N. K. Kildahl and D. H. Busch, *J. Coord. Chem., 10,* 85 (1980).

12 D. J. Olszanski and G. A. Melson, *Inorg. Chim. Acta, 26,* 263 (1978);
M. G. B. Drew, J. de O. Cabral, M. F. Cabral, F. S. Esho and S. M. Nelson, *J. Chem. Soc., Chem. Commun.,* 1033 (1979).

13 D. J. Olszanski and G. A. Melson, *Inorg. Chim. Acta, 23,* L4 (1977).

14 G. F. de Sá and M. A. V. de Almeida, *J. Coord. Chem., 10,* 35 (1980).

15 C. Cairns, S. G. McFall, S. M. Nelson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.,* 446 (1979).