

The Observation of Long Range Substituent Effects in Cadmium Schiff Base Complexes by Cadmium-113 NMR Spectroscopy

ELMER C. ALYEA

(GWC)², Guelph Campus, University of Guelph, Guelph, Ont. N1G 2W1, Canada

Received November 24, 1982

The coordinating ability of 2,6-diacetylpyridinebis(imines), (Fig. 1) terdentate NNN donor ligands derived by the Schiff base condensation of 2,6-diacetylpyridine with some aromatic amines, has been of continuing interest in our laboratory [1]. The characterization of pentacoordinate and octahedral nickel(II) complexes of these NNN donor ligands demonstrated their similarity to 2,2',2''-terpyridine (terpy), but did not differentiate the ligands with respect to their ligand field strengths [2]. The present investigation of cadmium complexes of the types CdX_2L and $[CdL_2]Y_2$ shows that the difference in electronic effects of the *para*-substituents in the 2,6-diacetylpyridinebis(imines) is observable by Cd-113 NMR spectroscopy.

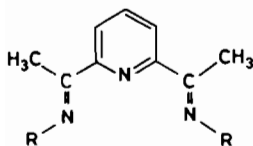


Fig. 1. Structural formula for 2,6-diacetylpyridinebis(imines).



The ¹¹³Cd NMR spectral data obtained at 88.75 MHz are summarized in Table I. Chemical shifts are expressed as δ values in ppm (positive values are downfield) relative to aqueous 0.1 M $Cd(ClO_4)_2$ as external standard [3]. The five- and six-coordinate cadmium complexes, which are readily isolated following earlier procedures for divalent metal complexes [1, 2], show chemical shifts (Table I) in the +24 to +351 ppm range, as expected for species with nitrogen, oxygen and halide donor ligands [4, 5].

The utility of ¹¹³Cd NMR spectroscopy, with a chemical shift range of nearly 900 ppm, has found wide application in recent years, particularly as a sensitive probe of metal ion sites in biologically-impor-

TABLE I. ¹¹³Cd NMR Chemical Shifts^a.

Complex ^b	δ ¹¹³ Cd(ppm)
CdCl ₂ (I)	350.7
CdCl ₂ (IV)	349.6
CdCl ₂ (II)	348.9
Cd(NCS) ₂ (IV)	295.1
[Cd(I) ₂](NO ₃) ₂	289.2
[Cd(IV) ₂](BF ₄) ₂	233.2
CdI ₂ (IV)	270.1
Cd(OAc) ₂ (IV)	69.1(72.4) ^c
Cd(NO ₃) ₂ (I)	26.6(24.1) ^c

^aPositive values are at higher frequency relative to external aqueous 0.1 M $Cd(ClO_4)_2$ at ambient probe temperature. Spectra were recorded on a Bruker WH-400 spectrometer operating at 88.75 MHz in the FT mode. Typically both the number of scans and the peak widths at half height were ca. 50. ^bSee Fig. 1 for ligands. ^cIn CH_3CN solution (values in parenthesis), otherwise in CH_2Cl_2 solution.

tant compounds [2–6]. The expected dependence of the chemical shift on the nature of the coordinated anion is shown for the present series of pentacoordinate $CdX_2(IV)$ complexes. The order of deshielding, $Cl > NCS > I > OAc$, is in agreement with previous observations of cadmium complexes containing these anions. The marked upfield resonances observed for the two complexes with coordinated oxygen atoms is normal, and indeed, by comparison with tri(pyridine) bis(*o*-hydroxybenzoate) (*i.e.* a 40,3N donor set with δ ¹¹³Cd = +61 ppm in the solid state [5]) even suggestive of seven coordination. Raman and infrared spectroscopic characterization [1] of $Cd(NO_3)_2(I)$ indicated though the presence of both monodentate and bidentate nitrate-groups, as proved by X-ray analysis for $Ni(NO_3)_2(I)$ [7].

A comparison of all the terdentate NNN donor ligands with respect to the influence of their substituents on the ¹¹³Cd resonance position was unfortunately not possible using the cationic complexes $[CdL_2]Y_2$ (L = (I)–(IV), Y = NO₃ or BF₄) since only two members of the series had sufficient solubility to allow their detection. The resonance position found for $[Cd(I)_2](NO_3)_2$ (289.1 ppm) is surprisingly similar to that reported [4] for the octahedral cation $[Cd(NH_3)_6]^{2+}$ (287 ppm). Signals due to $[Cd(III)_2](BF_4)_2$ or $CdCl_2(III)$, which had low solubilities even in DMSO solution, could not be discerned after 200 transients. Differentiation of the donor ability of the Schiff base ligands was however reflected in the ¹¹³Cd chemical shifts observed for the chloride complexes (Table I). The ligand with the methoxy-substituents provides the greater shielding, the ligand order being $II > IV > I$ (Fig. 1). The sensitivity of ¹¹³Cd NMR

spectroscopy as a probe to compare subtle differences in ligand coordinating abilities (that are not amenable to study with other divalent metals) is worthy of application to other areas of cadmium coordination chemistry. Our investigations of $\text{Cd}[\text{N}(\text{SiMe}_3)_2]_2 \cdot \text{L}'$ ($\text{L}' =$ monodentate ligands) systems as well as the range of CdX_2L and $[\text{CdL}_2]\text{Y}_2$ ($\text{L} = \text{I-IV}$) compounds will be reported in due course.

Acknowledgements

This work was supported by a Natural Sciences Engineering Research Council Canada operating grant. The technical assistance of Craig Maltby, a pre-first year student, in the syntheses of the complexes is gratefully acknowledged. Spectra were obtained by Mr. B. MacDonald at the Southwestern Ontario NMR

Centre funded by a Major Installation Grant from N.S.E.R.C.

References

- 1 E. C. Alyea, L. Ecott and P. H. Merrell, *Inorg. Chim. Acta*, **59**, 25 (1982) and references cited therein.
- 2 E. C. Alyea and P. H. Merrell, *Inorg. Chim. Acta*, **28**, 91 (1978).
- 3 R. G. Kidd and R. J. Goodfellow, in 'NMR and the Periodic Table', R. K. Harris and B. E. Mann, Eds., Academic Press, New York (1978), pp. 261.
- 4 R. A. Haberkorn, L. Que, Jr., W. O. Gillum, R. H. Holm, C. S. Liu and R. C. Lord, *Inorg. Chem.*, **15**, 2408 (1976).
- 5 P. F. Rodesiler and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 182 (1982).
- 6 P. F. Rodesiler, E. H. Griffith, P. D. Ellis and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 492 (1980) and references cited therein.
- 7 E. C. Alyea, G. Ferguson and R. J. Restivo, *Inorg. Chem.*, **14**, 2491 (1975).