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Characterization and Spectral Properties of Oxovanadium(IV), Palladium(II) and Lead(II) Complexes of Hemiporphyrazine

KAZUNORI SAKATA*, YU-ICHI HAYASHI,
KENJI GONDO and MAMORU HASHIMOTO

Department of Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata-ku, Kitakyushu 804, Japan

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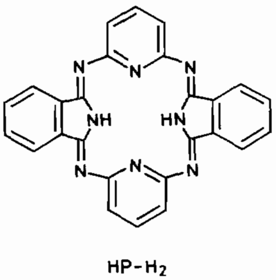
Although several metal derivatives of hemiporphyrazine ($HP-H_2$) have been reported, information on their spectral properties is sparse. Electrochemical and magnetic properties have been described for the manganese(II), cobalt(II) and copper(II) complexes of $HP-H_2$ [1]. Syntheses and properties of $[M(HP)O]_n$ polymers have also been published for the silicon and germanium complexes of $HP-H_2$ [2]. Recently Attanasio *et al.* reported the ESR study of the cobalt(II) and copper(II) complexes of $HP-H_2$ [3]. Elvidge and Linstead [4] and Honeybourne and Burchill [5] only reported the synthesis of the oxovanadium(IV) and lead(II) complexes with $HP-H_2$ without an investigation of spectral properties.

In the present work, we employed the oxovanadium(IV), palladium(II) and lead(II) complexes of $HP-H_2$ which is a 20π-macrocyclic ligand: 5,26:13,18-diimino-7,11:20,24-dinitrilodibenzo[*c,n*]-1,6,12,17-tetraazacyclodocosine. We report here the characterization and the structural features of the oxovanadium(IV), palladium(II) and lead(II) complexes of $HP-H_2$, as examined by electronic, vibrational, ESCA and ESR spectroscopy. The characteristic coordination behavior of the present 20π-macrocycle is discussed by reference to the ligand properties of the much more studied porphyrins and phthalocyanine.



$HP-H_2$

Experimental

Physical Measurements

Electron impact mass spectra for $HP-H_2$ and its oxovanadium(IV), palladium(II) and lead(II) complexes were recorded on a Shimadzu GCMS-9000 gas chromatograph–mass spectrometer at 70 eV, field desorption mass spectra for its oxovanadium(IV), palladium(II) and lead(II) complexes were carried out with a JEOL JMS-DX 300 gas chromatograph–mass spectrometer at 20–30 mA. Ultraviolet and visible spectra covering the 11 600–37 000 cm^{-1} range were taken on a Shimadzu UV-200S double-beam spectrophotometer for dimethyl sulfoxide solutions at room temperature. Infrared spectra in the region of 400–4000 cm^{-1} were performed on a JASCO IRA-2 grating spectrophotometer at room temperature, where a KBr disk method was used. ESCA spectroscopy was measured with a Du Pont 650B spectrometer utilizing a Mg Kα irradiation unit. A signal due to Au $4f_{5/2,7/2}$ was adopted for calibration. The ESR spectrum was obtained at room temperature on a JEOL JES-ME-1 X-band spectrometer equipped with a 100 kHz field modulation unit. The oxovanadium(IV) complex was doped in (≃1 wt.%) the isomorphous ligand ($HP-H_2$) for measurements. Manganese ion diffused into magnesium oxide was employed to acquire the standard reference signals for measurements. Melting points were observed on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. Elemental analyses were performed with a Yanaco CHN Corder MT-3. A Rigaku Denki TG-DSC differential thermobalance was used for the measurements of TG and DTA.

Preparation of Hemiporphyrazine

5,26:13,18-Diimino-7,11:20,24-dinitrilodibenzo[c,n]-1,6,12,17-tetraazacyclodocosine hydrate (1/1) ($HP-H_2 \cdot H_2O$)

This was prepared after the method of Esposito *et al.* [2a] from phthalonitrile (8.00 g) and 2,6-diaminopyridine (6.82 g) in 1-chloronaphthalene (70 ml). The crystalline solid was recrystallized from nitrobenzene to give yellow needles, yield 9.83 g (71%). *Anal.* Found: C, 68.11; H, 3.95; N, 24.13. Calc. for $C_{26}H_{16}N_8 \cdot H_2O$: C, 68.11; H, 3.96; N, 24.44%.

5,26:13,18-Diimino-7,11:20,24-dinitrilodibenzo[c,n]-1,6,12,17-tetraazacyclodocosine ($HP-H_2$)

The color of $HP-H_2 \cdot H_2O$ turned red on vacuum drying at 170 °C and $HP-H_2$ was isolated as red needles, melting point >300 °C. *Anal.* Found: C, 71.06; H, 3.82; N, 25.63 (M^+, 440). Calc. for C_{26}-

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*Author to whom correspondence should be addressed.

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$H_{16}N_8$: C, 70.90; H, 3.66; N, 25.44% (molecular weight 440.47).

(5,26:13,18-Diimino-7,11:20,24-dinitrilo-dibenzo[c,n]-1,6,12,17-tetraazacyclodocosinato)-oxovanadium(IV) (HP-VO)

This was prepared from oxovanadium(IV) sulfate pentahydrate (0.70 g) and $HP\text{-}H_2 \cdot H_2O$ (1.00 g) in *N,N*-dimethylformamide (15 ml) after Honeybourne and Burchill [5]. The product was recrystallized from nitrobenzene as glittering green needles; yield 0.81 g (54%), melting point >300 °C. *Anal.* Found: C, 62.04; H, 2.87; N, 22.09 (M^+, 505). Calc. for $C_{26}H_{14}N_8OV$: C, 61.79; H, 2.79; N, 22.17% (molecular weight 505.40).

(5,26:13,18-Diimino-7,11:20,24-dinitrilo-dibenzo[c,n]-1,6,12,17-tetraazacyclodocosinato)-palladium(II) (HP-Pd)

A mixture of palladium(II) chloride (0.49 g) and benzyl alcohol (20 ml) was added to $HP\text{-}H_2 \cdot H_2O$ (1.00 g) which was dissolved in boiling nitrobenzene (42 ml). The reaction mixture was heated under reflux with stirring for 2 h and allowed to cool. After filtration the solid residue was washed three times with methanol (5 ml) and then recrystallized from nitrobenzene to give glittering purple plates; yield 0.79 g (66%), melting point >300 °C. *Anal.* Found: C, 57.42; H, 2.65; N, 20.47 (M^+, 544). Calc. for $C_{26}H_{14}N_8Pd$: C, 57.31; H, 2.59; N, 20.57% (molecular weight 544.87).

(5,26:13,18-Diimino-7,11:20,24-dinitrilo-dibenzo[c,n]-1,6,12,17-tetraazacyclodocosinato)-lead(II) (HP-Pb)

The method of Elvidge and Linstead [4] was modified for the preparation of this complex. A mixture of lead(II) acetate trihydrate (1.04 g) and *N,N*-dimethylformamide (7.5 ml) was added to a slurry of $HP\text{-}H_2 \cdot H_2O$ (1.00 g) in hot *N,N*-dimethylformamide (7.5 ml). The reaction mixture was refluxed gently with stirring for 3.5 h and permitted to cool. The crystalline product was separated, washed three times with methanol (5 ml) and then recrystallized from nitrobenzene to give orange needles; yield 0.59 g (42%), melting point >300 °C. *Anal.* Found: C, 48.79; H, 2.03; N, 17.36 (M^+, 646). Calc. for $C_{26}H_{14}N_8Pb$: C, 48.37; H, 2.19; N, 17.36% (molecular weight, 645.65).

Results and Discussion

Characterization of Hemiporphyrazine

The TG and DTA curves indicated that yellow needles involve one hydrate water molecule. We have found that the yellow needles undergo dehydration with vacuum drying at 170 °C to give red needles and that the red needles also undergo hydration on heating in 50% aqueous methanol to give yellow needles. This equilibrium between yellow needles ($HP\text{-}H_2 \cdot H_2O$) and red needles ($HP\text{-}H_2$) is revealed by the following equation:

$$HP\text{-}H_2 \cdot H_2O \rightleftharpoons HP\text{-}H_2 + H_2O \qquad (1)$$

yellow needles   red needles

Mass Spectra

Mass spectral data for the macrocycle and its complexes are given in the 'Experimental' section. The EI mass spectra for the complexes show the presence of a molecular ion M^+ which is the base peak in the mass spectrum. The FD mass spectrum is shown in Fig. 1 for the lead(II) complex (HP-Pb) as an example. This exhibits the presence of molecular ions M^+ and M^{2+} which were also observed for the oxovanadium(IV) and the palladium(II) complexes.

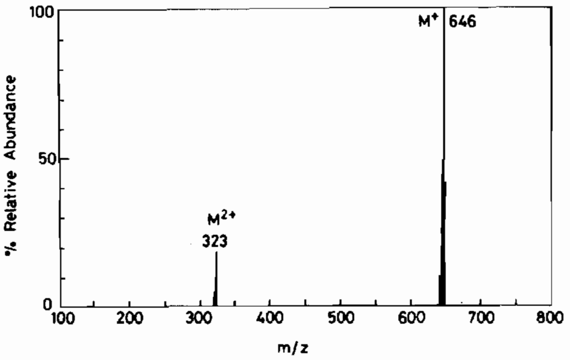

Fig. 1. Field desorption mass spectrum of the lead(II) complex (emitter heating current 20 mA).

Electronic Spectra

The electronic spectra covering the 15 000–40 000 cm^{-1} range are shown in Fig. 2 for the macrocycle and its oxovanadium(IV) and lead(II) complexes. The absorption bands appearing above 23 000 cm^{-1} are attributable to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and charge-transfer transitions from metal to ligand, since the molar extinction coefficients of the bands ($\sim 10^4$ mol^{-1} dm^3 cm^{-1}) are larger than those usually assigned to ligand-field transitions [6]. The general spectral behavior is similar to that observed for metal porphyrins [7]. A low intensity band observed at 17 200 cm^{-1} (ϵ 942) for the oxovanadium(IV) complex is due to a ligand-field transition [6]. This spectral behavior is consistent with a square-pyramid configuration. The palladium(II) complex is too insoluble to give a satisfactory electronic spectrum.

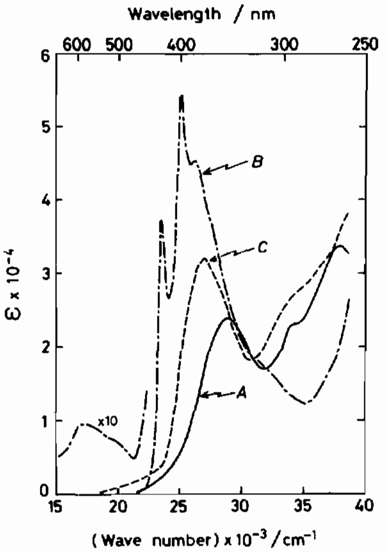

Fig. 2. Electronic absorption spectra for 5,26:13,18-diimino-7,11:20,24-dinitrilodibenzo[*c,n*]-1,6,12,17-tetraazacyclodocosine complexes at room temperature in dimethyl sulfoxide. (A) HP-H_2; (B) HP-VO; (C) HP-Pb.

TABLE 1. Characteristic IR Absorption Bands for 5,26:-13,18-Diimino-7,11:20,24-dinitrilodibenzo[*c,n*]-1,6,12,17-tetraazacyclodocosine Complexes[a, b]

Metal	IR band (cm^{-1})	Assignment
	1554(w)	ν(C=C)(conjugated ring)
	1557(m)	ν(C=C)(C=N)(macrocyclic skeletal)
	1665(s)	ν(C=N)
	3440(w)	ν(N–H)
VO(IV)	879(s)	ν(V=O)
	1540(w)	ν(C=C)(conjugated ring)
	1580(s)	ν(C=C)(C=N)(macrocyclic skeletal)
	1619(m)	ν(C=N)
Pd(II)	1564(w)	ν(C=C)(conjugated ring)
	1577(s)	ν(C=C)(C=N)(macrocyclic skeletal)
	1620(m)	ν(C=N)
Pb(II)	1546(m)	ν(C=C)(conjugated ring)
	1578(s)	ν(C=C)(C=N)(macrocyclic skeletal)
	1618(w)	ν(C=N)

[a] Measured by a KBr pellet technique at room temperature.
[b] Relative intensities: s, strong; m, medium; w, weak.

Vibrational Spectra

The characteristic IR bands are collected in Table 1. The metal-free macrocycle reveals a weak band at 3440 cm^{-1} which is dependent on an N–H stretching mode, as observed for the metal-free porphyrins [8]. This band mode vanishes on metal coordination. A strong band due to the stretching mode of the C=N bond without metal coordination turns up at 1665 cm^{-1}. This band is the most sensitive to metal coordination among the absorption peaks appearing in the 400–4000 cm^{-1} region and shifts to lower frequency upon complex formation. Such a spectral feature has been observed for metal porphyrins [9]. Oxovanadium(IV) porphyrin complexes exhibit strong V=O stretching frequencies around 1000 cm^{-1} [10]. On the other hand, a strong absorption band at 879 cm^{-1} observed for the present oxovanadium(IV) complex is attributed to the V=O stretching vibrational mode, because no band in this range was detected for the other metal complexes. The shift in the V=O stretching frequency has been considered to be an indication of an oxygen bridging, V–O–V, polymeric-chain formation [11].

ESCA Spectra

The present data are summarized in Table 2 which contains the binding energies of carbon (C $1s_{1/2}$) and nitrogen (N $1s_{1/2}$) along with those obtained for 5,10,15,20-tetraphenylporphine, phthalocyanine and their metal complexes [13, 14]. The present macrocycle shows two N ls peaks (396.8, 398.4 eV). The general spectral features of a nitrogen 1s peak are analogous to those observed for porphyrins and phthalocyanine [13–17]. Accordingly, there are two sorts of nitrogen atoms in the macrocycle: the one without a hydrogen atom and the other with hydrogen attached. As shown in Table 2, we find only one N 1s peak for the present macrocyclic complexes, that is, the four nitrogens are chemically equivalent in these complexes. The nitrogen 1s peak observed in the 397–399 eV range does not appreciably change the peak position on changing metal species. This result is similar to those obtained for

TABLE 2. Carbon 1s and Nitrogen 1s Core-electron Binding Energies for Macrocycles and their Metal Complexes[a]

Compound[b]	Binding energy (eV)		Reference
	C $1s_{1/2}$	N $1s_{1/2}$	
C atom	285		12
N atom		399	12
HP-H_2	282.4, 284.0	396.8, 398.4	this work
HP-VO	283.5	398.2	this work
HP-Pd	283.5	398.2	this work
HP-Pb	282.3, 283.8	397.9	this work
TPP-H_2	284.8	398.2, 400.2	13
TPP-Cu	284.8	398.9	13
PC-H_2	284.8, 286.2	398.9, 400.4	13
PC-VO		399.1	14
PC-Cu	284.8, 286.2	392.2	13

[a] Measured in the tablet state (5-mm diameter); for calibration, the signals of Au $4f_{5/2}$ and Au $4f_{7/2}$ were employed. [b] HP-H_2 = 5,26:13,18-diimino-7,11:20,24-dinitrilodibenzo[*c,n*]-1,6,12,17-tetraazacyclodocosine; TPP-H_2 = 5,10,15,20-tetraphenylporphine; PC-H_2 = phthalocyanine.

TABLE 3. Spin Hamiltonian Parameters for Oxovanadium(IV) Complexes of Macrocycles[a]

Complex	Medium[b]	$g_\parallel$	$g_\perp$	$A_\parallel^V \times 10^4$ (cm^{-1})	$A_\perp^V \times 10^4$ (cm^{-1})	Reference
HP-VO	HP-H_2	1.965	1.997	151.1	54.8	this work
PC-VO	PC-H_2	1.966	1.989	158	56	18
TPP-VO	TPP-H_2	1.966	1.985	161	55	19

[a] Measured at room temperature. Maximum possible errors: g, ± 0.0005; A^V, $\pm 0.5 \times 10^{-4}$ cm^{-1}. [b] See Table 2 for symbols for the ligands.

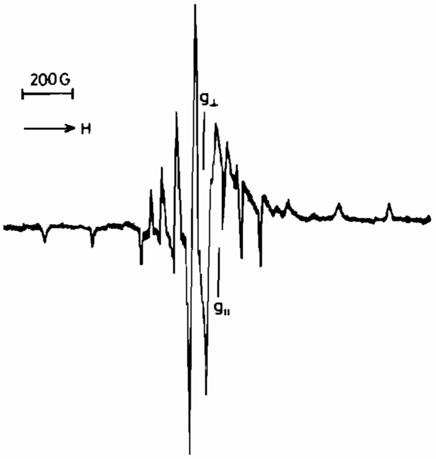

Fig. 3. ESR spectrum for the (5,26:13,18-diimino-7,11:-20,24-dinitrilodibenzo[*c*,*n*]-1,6,12,17-tetraazacyclodocosinato)oxovanadium(IV) complex magnetically diluted with the corresponding metal-free ligand at room temperature.

porphyrins [13, 15–17] and phthalocyanine [14].

ESR Spectra

The ESR spectrum of the oxovanadium(IV) complex magnetically diluted with the corresponding metal-free ligand at room temperature is shown in Fig. 3. This spectrum is made up of two sets of vanadium hyperfine lines, namely, $g_\parallel$ and $g_\perp$ components. The spectral features are similar to that observed for the oxovanadium(IV) complexes derived from phthalocyanine [18] and porphyrins [19–21]. The spin Hamiltonian parameters are practically consistent with those of the oxovanadium(IV) complexes, taken from refs. 18–21, as seen in Table 3. The superhyperfine splitting based on magnetic interaction between an unpaired electron in vanadium(IV) and nitrogen nuclei ($I = 1$) has not been observed in the present oxovanadium(IV) complex. Consequently, the present oxovanadium(IV) complex is of a square-planar type with an unpaired electron in the d_{xy} orbital.

Conclusions

The strong absorption bands appearing in the energy region greater than 23000 cm^{-1} for the oxovanadium(IV) and lead(II) complexes were attributed to $\pi \rightarrow \pi^*$ transitions within a ligand molecule and CT transitions from metal to ligand. The metal complexes assume the square-planar types. A strong band appearing at 1665 cm^{-1} was assigned to the C=N stretching mode and upon complex formation this band was shifted to lower frequency. A V=O stretching band for the oxovanadium(IV) complex was observed at 879 cm^{-1}. The EI mass spectra did not exhibit the presence of M^{2+} for these complexes but the FD mass spectra did. These complexes revealed a single nitrogen 1s peak by virtue of ESCA spectroscopy, whereas the metal-free hemiporphyrazine showed double nitrogen 1s peaks. The measured $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ values for the oxovanadium(IV) complex are similar to those observed for porphyrins and phthalocyanine. Judging from these values, the oxovanadium(IV) complex is in C_{4v} coordination symmetry with an unpaired electron in the d_{xy} orbital.

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References

1 (a) C. G. Birch and R. T. Iwamoto, *Inorg. Chim. Acta, 6* (1972) 680; (b) C. G. Birch and R. T. Iwamoto, *Inorg. Chem., 12* (1973) 66; (c) C. L. Honeybourne and P. Burchill, *Inorg. Nucl. Chem. Lett., 10* (1974) 715.

2 (a) J. N. Esposito, L. E. Sutton and M. E. Kenney, *Inorg. Chem., 6* (1967) 1116; (b) G. Meyer, M. Hartmann and D. Woehrle, *Makromol. Chem., 176* (1975) 1919; (c) W. Hiller and J. Straehle, *Liebigs Ann. Chem.,* (1980) 1946; (d) M. Hanack, K. Mitulla, G. Pawlowski and L. R. Subramanian, *J. Organomet. Chem., 204* (1980) 315; (e) M. Hanack and G. Pawlowski, *Naturwissenschaften, 69* (1982) 266; (f) C. W. Dirk and T. J. Marks, *Inorg. Chem., 23* (1984) 4325.

3 (a) D. Attanasio, I. Collamati and E. Cervone, *Inorg. Chem., 22* (1983) 3281; (b) E. Agostinelli, D. Attanasio,

I. Collamati and V. Fares, *Inorg. Chem., 23* (1984) 1162.

4 J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, (1952) 5008.

5 C. L. Honeybourne and P. Burchill, *Inorg. Synth., 18* (1978) 44.

6 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd edn., 1984.

7 (a) K. M. Smith, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1975; (b) D. Dolphin, *The Porphyrins*, Vol. III, Academic Press, New York, 1978.

8 L. J. Boucher and J. J. Katz, *J. Am. Chem. Soc., 89* (1967) 1340.

9 H. Ogoshi, N. Masai, Z. Yoshida, J. Takemoto and K. Nakamoto, *Bull. Chem. Soc. Jpn., 44* (1971) 49.

10 J. G. Erdman, V. G. Ramsey, N. W. Kalenda and W. E. Hanson, *J. Am. Chem. Soc., 78* (1956) 5844.

11 (a) M. Mathew, A. J. Carty and G. J. Palenik, *J. Am. Chem. Soc., 92* (1970) 3197; (b) B. J. McCormick and R. A. Bozis, *Inorg. Chem., 10* (1971) 2806; (c) R. L. Farmer and F. L. Urbach, *Inorg. Chem., 13* (1974) 587; (d) K. Kasuga, T. Nagahara and Y. Yamamoto, *Bull. Chem. Soc. Jpn., 55* (1982) 2665.

12 K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgran and B. Lindberg, *Electron Spectroscopy for Chemical Analysis – Atomic, Molecular and Solid State Structure Studies by Means of Electron Spectroscopy*, Almqvist and Wiksell, Uppsala, 1967.

13 Y. Niwa, H. Kobayashi and T. Tsuchiya, *J. Chem. Phys., 60* (1974) 799.

14 Y. Niwa, H. Kobayashi and T. Tsuchiya, *Inorg. Chem., 13* (1974) 2891.

15 M. V. Zeller and R. G. Hayes, *J. Am. Chem. Soc., 95* (1973) 3855.

16 D. Karweik, N. Winograd, D. G. Davis and K. M. Kadish, *J. Am. Chem. Soc., 96* (1974) 591.

17 J. P. Macquet, M. M. Millard and T. Theophanides, *J. Am. Chem. Soc., 100* (1978) 4741.

18 J. M. Assour, J. Goldmacher and S. E. Harrison, *J. Chem. Phys., 43* (1965) 159.

19 J. M. Assour, *J. Chem. Phys., 43* (1965) 2477.

20 E. M. Roberts, W. S. Koski and W. S. Caughey, *J. Chem. Phys., 34* (1961) 591.

21 D. Kivelson and S. K. Lee, *J. Chem. Phys., 41* (1964) 1896.