Formation and Reaction of Trichloro Complexes of Bivalent Transition Metals in 1,2-Dichloroethane

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Trichloro complexes of some bivalent transition metals (M^{2+}) have been prepared in tetra-n-butylammonium chloride–1,2-dichloroethane solution saturated with the metal chlorides. Their chemical forms and reactions, and the effect of water, have been investigated by means of spectrophotometry and vapour-pressure osmometry at 25.0 °C. Copper(II) and cadmium(II) form monomeric tetrahedral trichloro complexes containing one water molecule, $NBu_4[MCl_3(H_2O)]$, whilst cobalt(II) forms a dimeric tetrahedral trichloro complex $[NBu_4]_2[Co_2Cl_6]$. Zinc(II) exists as a mixture of monomeric and dimeric forms. Manganese(II) and nickel(II) do not form trichloro complexes. Copper(II) forms a monomeric tetrachloro complex. Cobalt(II) forms a monomeric tetrachloro complex and a trichloromono(pyridine base) complex by reaction with NBu_4Cl and with pyridine base, respectively. The formation constants of the copper(II) and cobalt(II) complexes have been evaluated by means of spectrophotometry. The effect of water on the equilibria of the trichloro complexes of copper(II) and cobalt(II) is discussed.

In solvents with relatively high solvating ability the first-row transition-metal ions (M^{2+}) are present generally in the form of a solvated ion of octahedral configuration.[1,2] By the addition of halogenide ion (X^-), these ions form halogeno complexes successively up to tetrahalogeno complexes. The higher complexes such as tri- and tetra-halogeno have tetrahedral configurations,[1,2] and the trihalogeno-complexes in solvating solvents are co-ordinated by one solvent molecule (solv), $MX_3(solv)^-$. On the other hand, in a low dielectric non-solvating solvent, since the solvent molecule does not participate in the co-ordination, the number of ligands (three chloride ions) is not sufficient to form the tetrahedral monomeric trihalogeno complex. Thus, the dimeric structure, $A_2[M_2X_6]$ (A^+ = counter cation), which is confirmed to be present in the crystalline state,[3] has been proposed.[1]

Water has a relatively high co-ordination ability [1] and acts as a base in acetic acid[4,5] and aprotic solvents.[6] Small amounts of water contained as an impurity in a poor solvating solvent often have serious effects on the complex-formation equilibria. The concentration of the impurity water is usually higher than that of the complex in question even in a well dehydrated solvent. Thus, the water content makes a significant contribution to the complex formation in a non-aqueous solvent.

In the present paper, the trichloro complexes of some bivalent transition metals were prepared in 1,2-dichloroethane, and their reactions with chloride ion, water, and pyridine bases were investigated at 25.0 °C by means of spectrophotometry and vapour-pressure osmometry.

Experimental

Reagents.—1,2-Dichloroethane was dehydrated with molecular sieve 3A (Wako) and distilled. The concentration of water in the dehydrated solvent was determind as about 10^{-3} mol dm^{-3} by the Karl–Fisher method and then the concentration was adjusted by adding water as necessary. The water concentration, c_{H_2O}, in this solvent when saturated with water is 1.7×10^{-1} mol dm^{-3} at 25.0 °C. All the anhydrous metal chlorides were of G.R. grade (Wako) and used as received. Tetra-n-butylammonium chloride was of analytical grade (Tokyo Kasei) and its purity was checked by titration with silver nitrate. The water content of NBu_4Cl was determined by the Karl–Fisher method.

Measurements.—A quantity of 1,2-dichloroethane containing NBu_4Cl (0.001—0.02 mol dm^{-3}) was shaken with several grams of crystalline anhydrous metal chloride at 25.0 °C for 30 min. This shaking time was found sufficient to saturate the metal chlorides. The saturated supernatant separated from the crystals by centrifugation was stored. An aliquot of the stock solution was evaporated and the residue was dissolved in distilled water. The concentrations of the metal and chloride ions were determined by titrations with ethylenediaminetetra-acetate (edta) and with silver nitrate, respectively. Spectrophotometric and vapour-pressure osmometric measurements were performed with a Shimadzu double-beam spectrophotometer UV-200 and an Hitachi model 117 molecular-weight apparatus, respectively. The degree of polymerization of the metal complex was evaluated from it's van't Hoff coefficient obtained by osmometry. Volatile substances such as water cause no vapour pressure depression, *i.e.* the van't Hoff coefficient of water is observed to be zero. All solutions were prepared under a dry nitrogen atmosphere, and all measurements were carried out at 25.0 °C.

Results and Discussion

Copper(II) *Complex.*—The ratio of the total chloride ion concentration (c_{Cl}) to that of total copper(II) ion (c_{Cu}) in the NBu_4Cl–1,2-dichloroethane solution saturated with anhydrous copper(II) chloride was determined as $c_{Cl}/c_{Cu} = 3.0 \pm 0.1$ at NBu_4Cl concentrations in the range 0.001—0.02 mol dm^{-3}. Osmometric molecular-weight measurements of the complex in the saturated solution revealed the degree of polymerization of copper(II) to be 0.92 ± 0.1 (c_{Cu} = 0.002—0.02 mol dm^{-3}). These results suggest the formation of a monomeric copper(II) complex, $NBu_4[CuCl_3]$.

As shown in Figure 1(*a*), curve 1, the u.v.–visible spectrum of the trichlorocuprate(II) complex has absorption maxima at 258, 324, and 475 nm. The addition of NBu_4Cl to a solution of this complex gives rise to the spectral changes shown in Figure 1(*a*). These spectra have isosbestic points at 272, 313, 382, and 451 nm and thus suggest the existence of a single equilibrium. The spectrum at the highest chloride concentration (curve 7) is that of $[CuCl_4]^{2-}$.[7,8] A plot of the apparent molar absorption coefficient, $\bar{\varepsilon}$, of the solution at 410 nm as a function of the molar ratio c_{Cl}/c_{Cu} is shown in Figure 2(*a*). These results indicate the

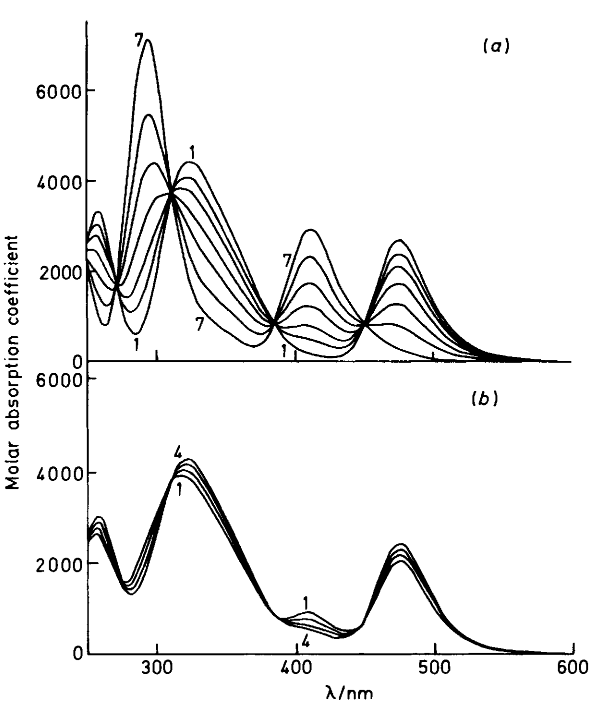

Figure 1. Absorption spectra of (*a*) copper(II) chloride containing various amounts of NBu_4Cl at $c_{H_2O} = 5 \times 10^{-2}$, $c_{Cu} = 3.33 \times 10^{-4}$ mol dm^{-3}, and c_{Cl}/c_{Cu} = 3.00 (curve 1), 3.21 (2), 3.36 (3), 3.66 (4), 3.98 (5), 4.45 (6), and 7.01 (7), and (*b*) of copper(II) chloride at various concentrations of water, $c_{Cu} = 2.42 \times 10^{-4}$, $c_{Cl} = 8.46 \times 10^{-4}$, and c_{H_2O} 5.0×10^{-3} (curve 1), 1.9×10^{-2} (2), 3.7×10^{-2} (3), and 5.8×10^{-2} mol dm^{-3} (4)

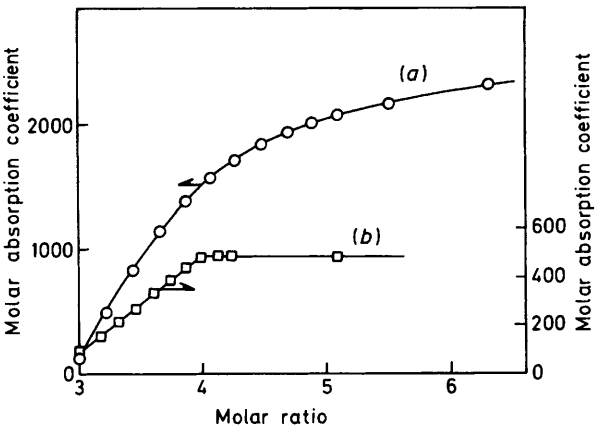

Figure 2. Plot of the apparent molar absorption coefficient of the copper(II) complex at 410 nm (*a*) and the cobalt(II) complex at 635 nm (*b*) as a function of the molar ratio c_{Cl}/c_M. $c_{Cu} = 7.34 \times 10^{-4}$, $c_{Co} = 1.01 \times 10^{-3}$ mol dm^{-3}

existence of equilibrium (1). As the dielectric constant of the

$$NBu_4[CuCl_3] + NBu_4Cl \xrightleftharpoons{K'_{Cl}(Cu)} [NBu_4]_2[CuCl_4] \quad (1)$$

solvent 1,2-dichloroethane is low (10.8 at 25.0 °C), the electrolytes are present in the form of ion pairs such as $NBu_4{}^+Cl^-$, $NBu_4{}^+[CuCl_3]^-$, and $2NBu_4{}^+[CuCl_4]^{2-}$. The apparent molar absorption coefficient, $\bar{\varepsilon}$, is given by equation (2), where ε_3, ε_4, and $K'_{Cl}(Cu)$ refer to the molar absorption coefficients of the tri- and tetra-chloro complexes and the equilibrium constant of equation (1), respectively. By rearrangement of equation (2) we

$$\bar{\varepsilon} = \{\varepsilon_3(NBu_4[CuCl_3]) + \varepsilon_4([NBu_4]_2[CuCl_4])\}/c_{Cu}$$
$$= \frac{\varepsilon_3 + \varepsilon_4 K'_{Cl}[NBu_4Cl]}{1 + K'_{Cl}[NBu_4Cl]} \quad (2)$$

obtained equation (3). A plot of the left-hand side of equation (3)

$$\log(\bar{\varepsilon} - \varepsilon_3)/(\varepsilon_4 - \bar{\varepsilon}) = \log K'_{Cl} + \log[NBu_4Cl] \quad (3)$$

as a function of log $[NBu_4Cl]$ is a straight line with a slope of unity, where $[NBu_4Cl]$ $\{= c_{Cl} - 3c_{Cu} - [(NBu_4)_2CuCl_4]\}$ is evaluated by using the relation $[(NBu_4)_2CuCl_4]/[(NBu_4)CuCl_3] = (\bar{\varepsilon} - \varepsilon_3)/(\varepsilon_4 - \bar{\varepsilon})$.[9] The equilibrium constant was obtained from the intercept of the plot as log $K'_{Cl}(Cu)$ = 3.39 at 5×10^{-2} mol dm^{-3} water. The solid line in Figure 2(*a*) is the calculated curve obtained by using this value.

The formation of the chloro complexes of copper(II) has been widely investigated in many non-aqueous solvents such as acetic acid,[10–12] acetonitrile,[13,14] dimethylformamide,[15,16] dimethyl sulphoxide,[17,18] propylene carbonate,[18] tetrahydrofuran,[19] trimethyl phosphate,[13,20] and methylene chloride[21] by means of spectrophotometry, potentiometry, *etc.* Furlani and Morpurgo[22] have assigned the absorption bands to the halogeno complexes $[CuX_n(solv)_{4-n}]^{2-n}$ in some non-aqueous solvents. Recent studies by Vierling and co-workers[12,16,18–20] showed the formation of monomeric trichloro complexes containing one solvent molecule, $[CuCl_3(solv)]^-$. According to these results, the trichloro complexes of copper(II) in these solvents have three absorption maxima in the u.v.–visible region, *e.g.* at 257, 310, and 440 nm in trimethyl phosphate[20] and at 253, 318, and 475 nm in tetrahydrofuran.[19]

The co-ordination number 'three' is extremely uncommon for copper(II),[8] especially in solution. Thus, it is anticipated that the monomeric species, $[CuCl_3]^-$, having absorption maxima at 258, 324, and 475 nm in 1,2-dichloroethane [Figure 1(*a*), spectrum 1] is tetrahedral, $[CuCl_3(solv)]^-$, as formed in other non-aqueous solvents as mentioned above. Because of the extremely low solvation ability of 1,2-dichloroethane,[1] its co-ordination is less important.

The u.v.–visible spectral change upon the addition of water at constant c_{Cl}/c_{Cu} (= 3.5) is shown in Figure 1(*b*). These spectra have the same isosbestic points as shown in Figure 1(*a*), and no significant new absorption band exists. The spectral change caused by the addition of water is the same as that caused by the decrease in NBu_4Cl concentration in Figure 1(*a*). These facts clearly indicate the participation of water, which is present in the solution as an impurity, in the complex-formation equilibrium (1). Considering the formation of the tetrahedral monoaquatrichlorocuprate(II) complex, $NBu_4[CuCl_3(H_2O)]$, the equilibrium (1) can be rewritten as in equation (4). Thus,

$$NBu_4[CuCl_3(H_2O)] + NBu_4Cl \xrightleftharpoons{K_{Cl}(Cu)} [NBu_4]_2[CuCl_4] + H_2O \quad (4)$$

the conditional constant $K'_{Cl}(Cu)$ is a function of the water concentration [equation (5)]. It was measured at various

$$\log K'_{Cl}(Cu) = \log K_{Cl}(Cu) - \log[H_2O] \quad (5)$$

concentrations of water ($c_{H_2O} = 5 \times 10^{-3}$—$5.8 \times 10^{-2}$ mol dm^{-3}). As the total concentration of water is much higher than that of copper(II), the free concentration of water can be approximated by the total concentration, c_{H_2O}. Although the slope of a plot of log $K'_{Cl}(Cu)$ *vs.* log c_{H_2O} (slope = 0.8) was somewhat lower than the theoretical slope of unity, $K'_{Cl}(Cu)$

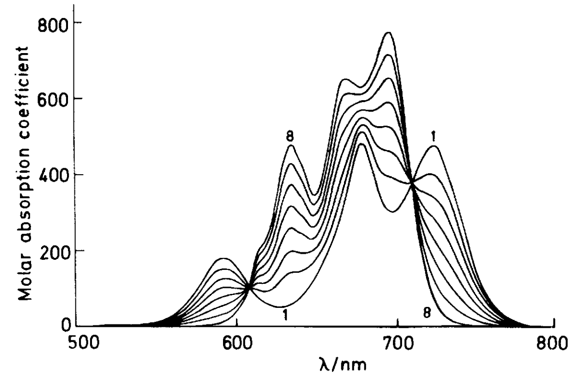

Figure 3. Absorption spectra of cobalt(II) chloride at various NBu_4Cl concentrations. $c_{Co} = 1.00 \times 10^{-3}$ mol dm^{-3}; $c_{Cl}/c_{Co} = 3.00$ (curve 1), 3.18 (2), 3.32 (3), 3.46 (4), 3.60 (5), 3.77 (6), 3.86 (7), and 4.00 (8)

shows a good correlation with the water concentration. The lower slope might be attributed to the decrease in activity of monomeric free water caused by the polymerization of water.

Lutwig and Textor[21] reported the formation of monomeric trihalogeno complexes of copper(II) in methylene chloride and in methylene bromide solution, and suggested that these complexes have trigonal planar structures with a co-ordination number of three. They, however, paid no attention to the concentration of water in the solvent. The absorption spectrum of the complex in methylene chloride is essentially the same as that of the trichloro complex in 1,2-dichloroethane presented here. Consequently, it is considered that the trichloro complex formed in methylene chloride (and in the bromide system, too) is the same as that presented here, $[CuCl_3(H_2O)]^-$.

Cobalt(II) *Complex.*—The ratio of the chloride-ion concentration (c_{Cl}) to that of cobalt(II) ion (c_{Co}) in the NBu_4Cl–1,2-dichloroethane solution saturated with anhydrous cobalt(II) chloride was determined as $c_{Cl}/c_{Co} = 3.1 \pm 0.1$. The molecular weight of the complex in the saturated solution yielded the degree of polymerizaton as 2.1 ($c_{Co} = 3.12 \times 10^{-3}$ mol dm^{-3}). These results suggest the formation of the dimeric trichloro complex, $[NBu_4]_2[Co_2Cl_6]$.

Bobbitt and Gladden[23] studied the equilibria of cobalt(II) chloride in acetonitrile by means of osmometry. They measured the effective molecular weight of cobalt(II) chloride as a function of concentration ($c_{CoCl_2} = 0.01$—0.3 mol dm^{-3}) and reported that the trichloro complex of cobalt(II) exists predominantly in dimeric form at the higher cobalt(II) chloride concentrations. Since these solutions contain other chloro complexes, the spectrum of the dimeric trichloro complex alone was not obtained.

The absorption spectrum of the trichloro complex is shown in Figure 3, curve 1. The spectrum scarcely changes upon changing the metal concentration. Thus, the dimeric structure is maintained even at metal concentrations as low as 2×10^{-4} mol dm^{-3}. The spectral change upon the addition of NBu_4Cl to the complex is also shown in Figure 3. These spectra have isosbestic points at 608 and 710 nm. The spectra at higher chloride concentrations ($c_{Cl}/c_{Co} > 4$) are that of a monomeric tetrachloro complex of cobalt(II), $[CoCl_4]^{2-}$.[7,9,24–27] The apparent molar absorption coefficient at 634 nm is plotted against c_{Cl}/c_{Co} in Figure 2(*b*). These results indicate the equilibrium (6). The

$$[NBu_4]_2[Co_2Cl_6] + 2NBu_4Cl \xrightleftharpoons{K_{Cl}(Co)} 2[NBu_4]_2[CoCl_4] \quad (6)$$

very sharp change in the slope of the plot of $\bar{\varepsilon}$ *vs.* c_{Cl}/c_{Co} at 4

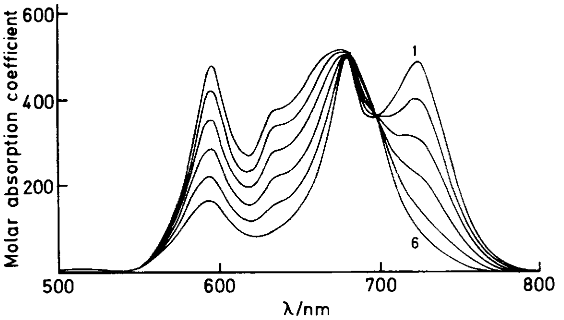

Figure 4. Absorption spectra of cobalt(II) chloride at various 4-cyanopyridine concentrations. $c_{Co} = 9.60 \times 10^{-4}$, $c_{Cl} = 2.89 \times 10^{-3}$ mol dm^{-3}; $c_{cpy}/c_{Co} = 0.00$ (curve 1), 0.242 (2), 0.428 (3), 0.610 (4), 0.791 (5), and 1.06 (6)

[Figure 2(*b*)] suggests that the equilibrium constant $K_{Cl}(Co) = [(NBu_4)_2CoCl_4]^2[(NBu_4)_2Co_2Cl_6]^{-1}[NBu_4Cl]^{-2}$ is very large.

The addition of 4-cyanopyridine (cpy) to the solution of the trichloro complex causes the spectral change shown in Figure 4. The spectrum at high cpy concentration is very close to that of the monomeric (4-cyanopyridine)trichloro complex $NBu_4[CoCl_3(cpy)]$.[9] Thus, the reaction with cpy is as in equation (7).

$$[NBu_4]_2[Co_2Cl_6] + 2(cpy) \xrightleftharpoons{K_{cpy}(Co)} 2NBu_4[CoCl_3(cpy)] \quad (7)$$

Generally, the lower the basicity of the pyridine base the smaller the adduct formation constant becomes.[9] The use of the very weak base cpy ($pK_a = 1.88$) makes it possible to evaluate the equilibrium constant $K_{cpy}(Co) = [(NBu_4)CoCl_3(cpy)]^2[(NBu_4)_2Co_2Cl_6]^{-1}[cpy]^{-2}$ as $\log K_{cpy}(Co) = 6.97$ by using the relation $[(NBu_4)_2Co_2Cl_6]/[(NBu_4)CoCl_3(cpy)] = (\varepsilon_{cpy} - \bar{\varepsilon})(2\bar{\varepsilon} - \varepsilon_d)$, where ε_d and ε_{cpy} are the molar absorption coefficients of the trichloro and monocyanopyridine complexes, respectively. The equilibrium constant of equation (8) has been

$$NBu_4[CoCl_3(cpy)] + NBu_4Cl \xrightleftharpoons{K_4(Co)} [NBu_4]_2[CoCl_4] + cpy \quad (8)$$

obtained as $\log K_4(Co) = 1.59$ for cpy.[9] By using the relation $K_{Cl}(Co) = K_{cpy}(Co) \cdot K_4(Co)^2$, we obtained the formation constant of tetrachlorocobaltate(II) from the trichloro complex as $\log K_{Cl}(Co) = 10.15$.

The addition of water to the solution of the dimeric trichloro complex of cobalt(II) results in a spectral change and precipitation. The spectrum of the supernatant at high water concentration is the same as that of the monomeric tetrachlorocobaltate(II) complex and the absorbance is just half that expected from the initial concentration of cobalt(II). These results suggest the disproportionation reaction (9).

$$[NBu_4]_2[Co_2Cl_6] + nH_2O \longrightarrow [NBu_4]_2[CoCl_4] + [CoCl_2(H_2O)_n]\downarrow \quad (9)$$

Other Metal Complexes.—By the same manner as that for the copper(II) and cobalt(II) complexes, the NBu_4Cl–1,2-dichloroethane solution was saturated with anhydrous manganese(II), nickel(II), zinc(II), and cadmium(II) chlorides. The molar ratio of chloride to Mn^{II} and Ni^{II} was determined as $c_{Cl}/c_M = 4.0 \pm 0.04$. The osmometric measurements of the solutions indicate the formation of monomeric complexes. Thus, the species in the saturated solutions is estimated to be $[NBu_4]_2[MCl_4]$ for Mn^{II} and Ni^{II}.

The molar ratios of chloride ion to Zn^{II} and Cd^{II} in the metal-saturated solutions were determined as $c_{Cl}/c_M = 2.56$ and 3.16, respectively. The osmometric measurements of these solutions indicate a degree of polymerization of 1.5 for Zn^{II} ($c_{Zn} = 1.35 \times 10^{-3}$ mol dm^{-3}) and 1.1 for Cd^{II} ($c_{Cd} = 1.02 \times 10^{-3}$ mol dm^{-3}). Thus, the formation of the monomeric trichloro complex is expected for cadmium(II), where one molecule of water may co-ordinate to the complex in the same manner as in the trichlorocuprate(II) complex, whereas in the case of zinc(II) the formation of both monomeric and dimeric complexes is anticipated. The formation of dimeric chloro complexes of zinc(II)[28,29] has been reported in acetic acid. Unfortunately, these complexes have no absorption band in the u.v. and visible region, and their solubility is too low to analyse the solution equilibria in detail.

References

1 V. Gutmann, 'Coordination Chemistry in Non-aqueous Solutions,' Springer, New York, 1968.
2 R. L. Carlin, 'Transition Metal Chemistry,' Marcel Dekker, New York, 1965.
3 A. F. Wells, 'Structural Inorganic Chemistry,' 4th edn., Oxford University Press, Oxford, 1975.
4 K. Sawada and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1975, **35**, 2455.
5 K. Sawada, K. Agata, and M. Tanaka, *Inorg. Chim. Acta*, 1978, **30**, 127.
6 M. M. Davis, in 'The Chemistry of Non-aqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York, 1970.
7 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984.
8 D. W. Smith, *Coord. Chem. Rev.*, 1976, **21**, 93.
9 K. Sawada and T. Suzuki, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2301.
10 R. P. Eswein, E. S. Howald, R. A. Howald, and D. P. Keeton, *J. Inorg. Nucl. Chem.*, 1967, **29**, 437.
11 K. Sawada, H. Ohtaki, and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3455.
12 M. A. Kahn, J. Meullemeestre, M-J. Schwing, and F. Vierling, *Polyhedron*, 1983, **2**, 459.
13 M. Bazz, V. Gutmann, G. Hampel, and J. R. Masaguer, *Monatsh. Chem.*, 1962, **93**, 1416.
14 S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4**, 1409.
15 H. Hubacek, B. Stancie, and V. Gutmann, *Monatsh. Chem.*, 1963, **94**, 1118.
16 M. Elleb, J. Meullemeestre, M-J. Schwing, and F. Vierling, *Inorg. Chem.*, 1980, **19**, 2699.
17 T. E. Saurez, R. T. Iwamoto, and J. Kleinberg, *Inorg. Chim. Acta*, 1973, **7**, 292.
18 M. Elleb, J. Meullemeestre, M-J. Schwing, and F. Vierling, *Inorg. Chem.*, 1982, **21**, 1477.
19 C. Amuli, J. Meullemeestre, M-J. Schwing, and F. Vierling, *Inorg. Chem.*, 1983, **22**, 3567.
20 C. Amuli, M. Elleb, J. Meullemeestre, M-J. Schwing, and F. Vierling, *Inorg. Chem.*, 1986, **25**, 856.
21 W. Lutwig and M. Textor, *Helv. Chim. Acta*, 1971, **54**, 1143.
22 C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, 1963, **1**, 102.
23 J. L. Bobbitt and J. K. Gladden, *Inorg. Chem.*, 1972, **11**, 2167.
24 D. A. Fine, *J. Am. Chem. Soc.*, 1962, **84**, 1139.
25 D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, 1960, **82**, 6013.
26 K. Sawada and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1974, **36**, 1971.
27 K. Sawada, T. Onoda, and T. Suzuki, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3263.
28 D. F. C. Morris, E. L. Short, and D. N. Waters, *J. Inorg. Nucl. Chem.*, 1963, **25**, 975.
29 K. Sawada, M. Okazaki, H. Hirota, and M. Tanaka, *Inorg. Chem.*, 1976, **15**, 1976.

Received 2nd *January* 1987; *Paper* 7/003