Inorganica Chimica Acta, 191 (1992) 103–107

The hydrolysis products of *cis*-diamminedichloroplatinum(II)
7. The rate of the hydrogen isotope exchange reaction

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(Received July 11, 1991; revised September 11, 1991)

Abstract

The rate of the N–H → N–D exchange reaction for *cis*-$PtCl_2(NH_3)_2$, $PtCl_2$(en) and $PtCl_2$(tn) has been measured in succinate buffered D_2O. Samples of the complex were precipitated as the $HgCl_2$ adduct, at various times, and the extent of deuteration was estimated by IR spectroscopy. The rate of the reaction is proportional to the [OD^-] and activation parameters for the three complexes (I=0.1 M NaCl, 25.0 °C) in the order $(NH_3)_2$, (en), (tn) are: $10^4\ k_{ex}$ ($M^{-1}\ s^{-1}$)=135, 51.4, 3.64; ΔH^{*} (kJ mol^{-1})=24.9, 21.2, 50.0; ΔS^{*} (J K^{-1} mol^{-1})= −44.1, −64.6, +10.2.

Introduction

Four-coordinate square-planar platinum(II) complexes, e.g. *cis*-$PtCl_2(NH_3)_2$ (*cis*-DDP), are widely used for the treatment of specific types of human cancer [1]. In the development and testing of such Pt-containing drugs it has been found that those containing and N–H group coordinated to Pt(II) are more active than those where this feature is absent [2]. As a consequence, it has been suggested that this N–H functional group is involved in hydrogen-bonding when the hydrolyzed Pt complex [3–6] interacts with donor groups in replicating DNA [7, 8].

However, it is also possible that there may be special kinetic features associated with such N–H protons as it is known that such protons are particularly acidic in Pt(IV) systems [9]. We now present the rate of hydrogen isotope exchange for *cis*-$PtCl_2(NH_3)_2$, $PtCl_2$(en) and $PtCl_2$(tn) which is an approximate measure of N–H acidity [10].

Experimental

Cis-$PtCl_2(NH_3)_2$ and K_2PtCl_4 were purchased from Strem Chemical Co. and $PtCl_2$(en) and $PtCl_2$(tn) were prepared from $PtCl_2(DMSO)_2$ using the literature procedures [11, 12]. D_2O (99.9 at.% D) was purchased from Aldrich Chemical Co. and all other chemicals were the best reagent grade available. IR spectra were recorded in KBr discs using a Perkin-Elmer 1600 FTIR which was also able to compute peak areas.

The glass electrode was calibrated with 0.05 *M* potassium hydrogen phthalate at the appropriate temperature [13].

Exchange rate measurements

Small samples of *cis*-$PtCl_2(NH_3)_2$, $PtCl_2$(en) or $PtCl_2$(tn) were sonically dissolved in D_2O containing succinic acid, disodium succinate and NaCl to give an ionic strength of 0.1 M. The solution was quickly filtered, adjusted to the appropriate temperature, the timer activated, and the pH measured using the calibrated glass electrode.

For example, a solution (26.0 ml D_2O) containing 0.0767 g succinic acid, 0.1755 g sodium succinate and 0.152 g NaCl was prepared. Half of this solution was heated to 40.0 °C and 15 mg of *cis*-DDP was added. After sonification, the measured pH of the filtered solution (at 40.0 °C) was 4.69, when the pH-meter glass electrode was calibrated (pH = 4.03) with 0.05 M potassium hydrogen phthalate at 40.0 °C. At suitable time intervals, 2.0 ml of reactant solution were removed and quenched with 1 M $HClO_4$ saturated with $HgCl_2$ (2.0 ml) and the $HgCl_2$ adduct [14] of *cis*-DDP (~2.4 mg, *cis*-DDP; ~0.5 mg, $PtCl_2$(en) or $PtCl_2$(tn)) deposited over 3–24 h at room temperature. After centrifugation, the mother liquor was removed by decantation and the precipitate was washed successively with ethanol and ether and air dried.

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0020-1693/92/$5.00

The dry weighed material was ground with KBr (150 mg) and 0.6 mm diameter discs were prepared in a hydraulic press. The FT-IR spectra were recorded with 4 iterations over the 4000–450 cm^{-1} region.

IR spectral analysis

All bands in the IR spectra of $[(cis\text{-}PtCl_2(NH_xD_{3-x})_2)_2(HgCl_2)_3]_n$ [14] showed changes with time and the loss of the 798 cm^{-1} band, corresponding to $[(cis\text{-}PtCl_2(NH_3)_2)_2(HgCl_2)_3]_n$, was used to estimate the reaction rate. The area (A) of this band was normalized to 1.0 mg of the adduct and plots of ln (area/mg sample)$_t$ versus t were linear for two half-lives. The slopes of these lines gave the k_{obs} data (Table 1).

The IR spectra of the $HgCl_2$ adduct of $PtCl_2(en\text{-}H_xD_{4-x})$ had one band at 1052 cm that was invariant with x and another at 1563 cm^{-1} that decayed to zero as the reaction proceeded. Plots of ln [peak height at 1563/peak height at 1052]$_t$ versus t were linear for two half-lives and k_{obs} values (Table 1) were calculated from the slopes. For $PtCl_2(tn)$ a similar procedure was used, employing bands at 2884 and 1574 cm^{-1} (invariant with time).

Conversion of k_{obs} to k_{ex}

The expression

$$k_{ex}=k_{obs}\,[OD^-]^{-1} \tag{1}$$

is used to calculate k_{ex} as the $[OD^-]$ is constant due to the added buffer. Thus, it is necessary to calculate $[OD^-]$ in D_2O ($I=0.1$ M) at various temperatures and pH (measured in D_2O, but calibrated with H_2O) – not a trivial exercise!

By definition:

$$K_w^{D_2O}=[D^+]\gamma D^+\cdot[OD^-]\gamma OD^-/aD_2O \tag{2}$$

therefore

$$-\log\{[D^+][OD^-]\}$$
$$=pK_{wc}^{D_2O}=-\log\left[K_w^{D_2O}\frac{aD_2O}{\gamma D^+\cdot\gamma OD^-}\right] \tag{3}$$

as tabulated $K_w^{D_2O}$ values pertain to zero ionic strength. We will assume that this activity–activity coefficient ratio in 0.1 M NaCl (D_2O) is the same as that for 0.1 *M* NaCl in H_2O [19].

Also from the definition:

$$-\log[OD^-]=pK_{wc}^{D_2O}-p[D^+] \tag{4}$$

$$=pK_{wc}^{D_2O}-\log\gamma\pm-(\text{pH-meter reading}+0.4) \tag{5}$$

The 0.4 is the standard 'D_2O' correction [15] and $\gamma\pm$ is the activity coefficient for D^+ in DCl ($I=0.1$ M) in D_2O. Again we assume this value is the same as the activity coefficient for H^+ in HCl ($I=0.1$ M) in H_2O [20]. These values, at the appropriate temperatures,

TABLE 1. Rate constants for the NH–ND exchange reaction of some square planar $PtCl_2$(diamine) complexes in D_2O at various pH and temperature ($I=0.1$ M)[a]

T °C [K]	pH[b, c] (meas.)	$p[D^+]$[d]	$10^4\times k_{obs}$ (s^{-1})	10^{10} $[OD^-]$[e] (M)	$10^{-4}\times k_{ex}$[f] (M^{-1} s^{-1})	$10^{-4}\times k_{ex}$ (calc.)[g] (M^{-1} s^{-1})
cis-PtCl$_2(NH_3)_2$						
25.0 [298.2]	4.40	4.80	1.57	1.12	141	135
	5.30	5.70	11.6	8.89	131	
32.0 [330.2]	4.63	5.03	5.57	3.26	171	174
40.0 [338.2]	4.65	5.05	14.0	6.14	228	229
	4.69	5.09	15.7	6.73	233	
$PtCl_2(en)$						
25.0 [298.2]	4.67	5.07	1.06	2.08	51.0	51.4
32.0 [330.2]	4.69	5.09	2.43	3.74	65.0	64.0
40.0 [338.2]	4.71	5.11	5.68	7.05	80.6	81.2
$PtCl_2(tn)$						
25.0 [298.2]	5.95	6.35	1.41	39.7	3.55	3.64
32.0 [330.2]	5.85	6.25	2.98	47.8	6.23	5.92
40.0 [338.2]	5.69	6.09	6.76	67.3	10.0	10.1
	5.19	5.59	2.10	21.3	9.86	
$Co(NH_3)_6^{3+}$[h]						
25.0 [298.2]	5.21	5.61	6.67	7.22	92.4[i]	

[a] All reaction solutions were 0.1 M in NaCl. [b] Calibrated with potassium hydrogen phthalate solution (0.05 M) at the appropriate temperature (pH=4.01, 25.0 °C; 4.02, 32 °C; 4.03, 40.0 °C) [13a]. [c] The pH was controlled with disodium succinate–succinic acid buffers (0.05 M) [13b] in D_2O ($I=0.1$ M NaCl) and measured with the calibrated glass electrode at the appropriate temperature. [d] $p[D^+]=pH+0.4$ [15]. [e] $-\log[OD^-]=pK_{wc}^{D_2O}-\log\gamma\pm-p[D^+]$ (see Table 2). [f] $k_{ex}=k_{obs}\,[OD^-]^{-1}$. [g] Calculated from the activation parameters cited in Table 3. [h] Precipitated as the *p*-toluene sulfonate salt [16] and using bands at 4.07 and 12.2 μ (invariant) to monitor the extent of deuteration. $[Co(NH_3)_6]Cl_3=3.33\times10^{-3}$ M in 0.1 M NaCl, $I=0.12$ M. [i] Other values reported are $10^{-4}k_{ex}=160$ [17], 120 [16] and 57 [18].

TABLE 2. Parameters used in the calculation of [OD$^-$]

T (°C)	$\frac{\gamma D^+ \times \gamma OH^-}{aD_2O}$ [a]	$pK_w^{D_2O}$ [b]	$pK_{wc}^{D_2O}$	$\gamma\pm$ [c]	log $\gamma\pm$	[$pK_{wc}^{D_2O}$ − log $\gamma\pm$] [d]
25.0	0.607	14.869	14.652	0.7964	−0.099	14.751
32.0 [e]	0.603	14.636	14.416	0.7931	−0.101	14.517
40.0	0.595	14.385	14.159	0.7891	−0.103	14.262

[a] Data from ref. 19 for H_2O. [b] From ref. 21. [c] $\gamma\pm$ for D^+ in DCl assumes same as $\gamma\pm$ for H^+ in HCl [20]. [d] Used to calculate [OD$^-$] in Table 1. [e] Extrapolated from ref. 20.

are listed in Table 2. Neglect of these activity coefficient corrections, e.g. by using p[OD$^-$]$=pK_w^{D_2O}-$p[D$^+$], results in a reduction of [OD$^-$] by 20–30%. Once [OD$^-$] is calculated, values for k_{ex} follow from eqn. (1) (Table 1).

If the 'D_2O correction' of 0.4 is also neglected i.e. by using p[OD$^-$]$=pK_w^{D_2O}-$pH measured, the [OD$^-$] drops by about 70%.

As a check on our procedures, we have also measured the proton exchange rate for $Co(NH_3)_6^{3+}$ using the IR method. Our value for $10^{-4}k_{ex}$ (25 °C, $I=0.12$ M) = 92.4 M^{-1} s^{-1} (Table 1), is in acceptable agreement with those determined previously [16–18].

Results and discussion

Inert transition-metal (M) amine complexes containing the M–NH functional group exchange N–H protons, when dissolved in D_2O, according to the rate law [18] -d(NH)/d$t=k_{ex}$[complex][OD$^-$].

At constant temperature and ionic strength, the rate of the reaction is controlled by the pD of the solution and at fixed pD, pseudo-first-order kinetics (k_{obs}) are observed where k_{obs}-k_{ex} [OD$^-$]. The contribution from other bases (buffer anions or water) to the exchange process (general base catalysis) is small, and plots of k_{obs} versus [OD$^-$] are generally linear and intercept close to the origin [16–18].

Several different techniques have been used to follow the reaction, which can be approached from two directions, either the fully deuterated complex in H_2O [16, 18, 22, 23] or the fully protonated complex in D_2O. Early investigators used the former procedure, as D_2O was expensive. The reaction was followed by either measuring the density increase in the solvent water as the reaction proceeded [18, 24] or precipitating the complex with a suitable anion, and measuring the decrease in deuteration using IR spectroscopy [16]. For NH_3 complexes, this latter procedure requires a calibration curve to be prepared using the complex equilibrated in various D_2O/H_2O mixtures, as the reaction proceeds through the sequence $ND_3 \rightarrow NHD_2 \rightarrow NH_2D \rightarrow NH_3$ and the IR spectrum at time t, will be a 'freeze-frame' of the mixture at that time.

As D_2O has become less expensive, procedures to measure the exchange reaction in D_2O have become more popular, especially those that do not involve separation of the complex from solution. NMR techniques, either monitoring the –OH resonance increase with time [25] or the –NH resonance decrease with time [26–30] have been used for diamagnetic complexes, and even line broadening measurements for paramagnetic complexes [31]. The appearance of an –OH band in the near IR spectrum (1600 nm) for amine complexes in buffered D_2O has been frequently used [22, 23, 25, 31–33]. Provided suitable precipitants can be obtained, the solid state IR method is also satisfactory [16, 34, 35] and is the method chosen in this work.

The IR spectrum of *cis*-$PtCl_2(ND_3)_2$ has been described previously [36, 37] and our samples of the fully deuterated *cis*-DDP gave spectra that corresponded with the literature. The IR spectra of $HgCl_2$ adducts of *cis*-$PtCl_2(NH_3)_2$ and *cis*-$PtCl_2(ND_3)_2$ have relatively few bands in the 450–4500 cm^{-1} region, but the IR spectra of partially deuterated samples are quite complicated.

In fact, we could follow the reaction progress, $NH_3 \xrightarrow{k_1} NH_2D \xrightarrow{k_2} NHD_2 \xrightarrow{k_3} ND_3$. As bands corresponding to NH_2D (1210 cm^{-1}) and NHD_2 (1076 cm^{-1}) appeared and disappeared. Our procedure monitored the loss of the NH_3 band (corresponding to k_1). A set of time versus concentration curves [38] based on the above sequence, where $k_1=2\times10^{-4}$ s^{-1} ($t_{1/2}\sim$ 1 h) $k_2=2/3$ k_1 and $k_3=1/3k_1$, modelled the observed profile (pD = 4.80, $T=25$ °C) indicating entirely statistical NH → ND displacements. This also means that it is not possible to monitor the reverse reaction ($ND_3 \rightarrow NH_3$), following the production of NH_3, as this is formed last in a sequential process.

Exchange rate comparisons

In this section we are now able to make ligand, metal center and charge type comparisons. Considerable discussion has occurred in the literature with regard to exchange rates in the series NH_3, en, tn for a particular metal center. This has been complicated by a confusing misinterpretation of the early work [18] where the

TABLE 3. Activation parameters [k_x[a], ΔH^{*} (kJ mol^{-1}), ΔS^{*} (J K^{-1} mol^{-1})] for reactions associated with dichlorodiamineplatinum(II) complexes (25.0 °C, I=0.1 M)

Reaction		*cis*-$PtCl_2(NH_3)_2$	$PtCl_2$(en)	$PtCl_2$(tn)	Reference
NH → ND exchange	k_{ex}	131×10^4	51.4×10^4	3.64×10^4	this work
	ΔH^{*}	24.9 ± 2	21.7 ± 2	50.0 ± 3	
	ΔS^{*}	-44 ± 4	-64 ± 4	$+10\pm6$	
Acid hydrolysis	k_H	5.24×10^{-5}	3.20×10^{-5}	5.88×10^{-5}	3
	ΔH^{*}	87.5 ± 3	97.1 ± 3	97.0 ± 3	
	ΔS^{*}	-34 ± 6	-5 ± 6	-1 ± 6	
Base hydrolysis	k_{OH}	1.90×10^{-5}			4
	ΔH^{*}	84.4 ± 4			
	ΔS^{*}	-52 ± 8			

[a] $k_x=k_{ex}$ (M^{-1} s^{-1}), k_H (s^{-1}) and k_{OH} (s^{-1}).

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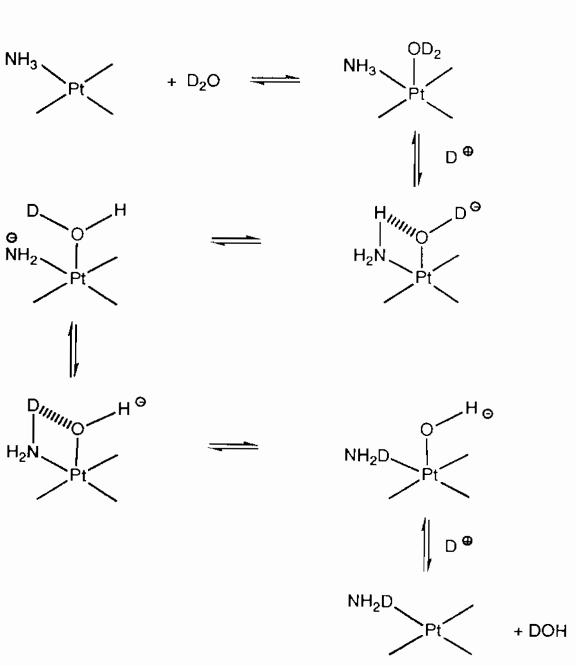

Scheme 1.

exchange rate for $Co(NH_3)_6^{3+}$ is found to be faster than that for $Co(en)_3^{3+}$, but the reverse has been cited in the later literature [17].

A survey of the available data [25, 39] suggests that there is little difference between k_{ex} for $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, but $Co(tn)_3^{3+}$ exchanges much more rapidly. This *not* the observed trend for the neutral Pt(II) complexes described here, where the relative rate order is $(NH_3)_2 >$ (en) $>$ (tn) in the ratio 36:14:1. (This ratio will be quite temperature dependent but the order will not change in the 0–100 °C range).

For square planar Pt(II) complexes, there is a potential exchange path that is not available for inert octahedral complexes viz. an associative water exchange process (Scheme 1) via five-coordinate intermediates. Consideration of the activation entropy for exchange, acid hydrolysis and base hydrolysis (Table 3) suggests parallel trends in the three complexes. Data are also available for exchange rates in square planar $Pt(NH_3)_4^{2+}$ (k_{ex}(25.0 °C) = 10.6×10^4 M^{-1} s^{-1}, ΔH^{*} = 45 ± 3 kJ mol^{-1}, ΔS^{*} = $+2\pm6$ J K^{-1} mol^{-1}) [24] and $Pt(en)_2^{2+}$ (k_{ex}(25.0 °C) = 16×10^4 M^{-1} s^{-1}) [39] where charge appears to have little effect [40–45]. The lack of charge discrimination observed for acid hydrolysis reactions in square planar Pt(II) systems has been used previously to support an associative water attack.

A similar proton exchange mechanism has recently been proposed [46] for the base-assisted *sec*-NH proton isomerization in square planar Ni(cyclam)$^{2+}$ systems.

The fact that the proton exchange rate for $PtCl_2$(tn) is about 10× less than that for *cis*-$PtCl_2(NH_3)_2$ almost certainly arises from structural (steric) effects. The N–Pt–N angle in the solid state is 97, 92 and 73° for Pt(mal)(Me_2tn) [47], *cis*-$PtCl_2(NH_3)_2$ [14] and $PtCl_2$(en) [48], respectively, and as this angle changes, so will the orientation of the N–H protons with respect to the bound axial water molecule.

Conclusions

We now consider the question that prompted this investigation. Is there anything remarkable about the *kinetic* behaviour of N–H protons bound to Pt(II) that would enhance the reactivity towards replicating DNA?

The direct answer appears to be, no. However, if structure making via H-bond formation is important in the binding of Pt(II) complexes to DNA and if the most labile N–H protons form the strongest hydrogen bonds, then *cis*-DDP will be the most effective of the three complexes studied, in using this property for binding.

Acknowledgements

We thank the New Zealand University Grants' Committee for funds to purchase instruments used in this research and Edward Koubek thanks the United States Naval Academy for sabbatical leave.

References

1 G. F. J. Barnard, M. J. Cleare and P. C. Hydes, *Chem. Br., 22* (1986) 1001.
2 N. Farrell, in R. Ugo and B. R. James (eds.), *Catalysis by Metal Complexes,* Vol. 11, Kluwer, Dordrecht, 1989, p. 1.
3 S. E. Miller and D. A. House, *Inorg. Chim. Acta, 161 (1989) 131.*
4 S. E. Miller and D. A. House, *Inorg. Chim. Acta, 166* (1989) 198.
5 S. E. Miller and D. A. House, *Inorg. Chim. Acta, 173* (1990) 53.
6 S. E. Miller, K. J. Gerard and D. A. House, *Inorg. Chim. Acta, 190* (1991) 135.
7 S. E. Sherman, D. Gibson, A. H.-J. Wang and S. J. Lippard, *Science, 203* (1985) 412; *J. Am. Chem. Soc., 110* (1988) 7368.
8 R. Faggiani, B. Lippert and C. J. L. Lock, *Inorg. Chem., 21* (1982) 3210, 3216.
9 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* Wiley, New York, 2nd edn., 1967, p. 33.
10 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* Wiley, New York, 2nd edn., 1967, p. 184.
11 R. Romeo, D. Minniti, S. Lanza and M. L. Tobe, *Inorg. Chim. Acta, 22* (1977) 87.
12 F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, R. Quaranta, M. Coluccia, L. Di Bari, D. Giordano and M. A. Mariggio, *Inorg. Chim. Acta, 137* (1987) 45.
13 D. D. Perrin and B. Dempsey, *Buffers for pH and Metal Ion Control,* Chapman and Hall, London, 1974, (a) p. 39; (b) p. 135.
14 S. E. Miller and D. A. House, *Inorg. Chim. Acta, 184* (1991) 111.
15 P. K. Glasoe and F. A. Long, *J. Am. Chem. Soc., 64* (1960) 188.
16 H. Block and V. Gold, *J. Chem. Soc.,* (1959) 966.
17 J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem., 15* (1960) 279.
18 J. S. Anderson, H. V. A. Briscoe and N. L. Spoor, *J. Chem. Soc.,* (1943) 361.
19 H. S. Harned and B. B. Owen, *Physical Chemistry of Electrolyte Solutions,* A.C.S. Monograph 137, Reinhold, New York, 3rd edn., 1958, p. 752, Table 15-2-1A.
20 H. S. Harned and B. B. Owen, *Physical Chemistry of ELectrolyte Solutions,* A.C.S. Monograph 137, Reinhold, New York, 3rd edn., 1958, p. 716, Table 11-4-1A.
21 R. C. Weast (ed.), *Handbook of Chemistry and Physics,* The Chemical Rubber Co., CRC Press, Cleveland, OH, 54th edn., 1973, D131; from NBS *Tech. Note 400.*
22 J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem., 15* (1960) 279.
23 J. W. Palmer and F. Basolo, *J. Phys. Chem., 64* (1960) 778.
24 J. S. Anderson, V. H. Briscoe, L. H. Cobb and N. L. Spoor, *J. Chem. Soc.,* (1943) 367.
25 F. Basolo, J. W. Palmer and R. G. Pearson, *J. Am. Chem. Soc., 82* (1960) 1073.
26 D. A. Buckingham, P. A. Marzilli and A. M. Sargeson, *Inorg. Chem., 8* (1969) 1595.
27 D. A. Buckingham, B. M. Foxman and A. M. Sargeson, *Inorg. Chem., 9* (1970) 1790.
28 D. A. Buckingham, P. J. Cresswell and A. M. Sargeson, *Inorg. Chem., 14* (1975) 1485.
29 G. Marangoni, M. Panayotou and M. L. Tobe, *J. Chem. Soc., Dalton Trans.,* (1989) 1973.
30 J. Lichtig, M. E. Sosa and M. L. Tobe, *J. Chem. Soc., Dalton Trans.,* (1984) 581.
31 R. G. Pearson, J. W. Palmer, M. M. Anderson and A. L. Allred, *Z. Elektrochem., 64* (1960) 110.
32 M. Parris and J. W. Wallace, *Inorg. Chem., 3* (1964) 133.
33 H. Yamatera and M. Fujita, *Bull. Chem. Soc. Jpn., 42* (1969) 3043.
34 D. A. House and O. Nor, *Inorg. Chim. Acta, 70* (1983) 13.
35 P. Kita, *Pol. J. Chem., 62* (1988) 653.
36 G. M. Barron, R. H. Krueger and F. Basolo, *J. Inorg. Nucl. Chem., 2* (1956) 340.
37 K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate and G. T. Behnke, *Inorg. Chem., 4* (1965) 36.
38 R. K. Harris and R. J. Morrow, *J. Chem. Soc., Faraday Trans. I, 80* (1984) 3071.
39 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions,* Wiley, New York, 2nd edn., 1967, p. 185, Table 3.23.
40 P. Haake and P. C. Turley, *J. Am. Chem. Soc., 90* (1968) 2293.
41 J. B. Goddard and F. Basolo, *Inorg. Chem., 8* (1969) 2223.
42 D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *J. Am. Chem. Soc., 91* (1969) 5227.
43 L. E. Erikson, A. J. Dappen and J. C. Uhlenhopp, *J. Am. Chem. Soc., 91* (1969) 2510.
44 L. E. Erikson, H. L. Fritz, R. J. May and D. A. Wright, *J. Am. Chem. Soc., 91* (1969) 2513.
45 L. E. Erikson, *J. Am. Chem. Soc., 91* (1969) 6284.
46 R. W. Hay and C. You-Quan, *Inorg. Chim. Acta, 180* (1991) 147.
47 C. G. van Kralingen, J. Reedijk and A. J. Spek, *Inorg. Chem., 19* (1980) 1481.
48 J. Iball, M. MacDougall and S. Scrimgeour, *Acta Crystallogr., Sect. B, 31* (1975) 1672.