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The Synthesis and Crystal Structures of Two Cobalt(III) Complexes Containing the Ligand 1,4,8,11-Tetraazacyclotetradecane

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The new cobalt(III) complex $[Co(cyclam)(NO_3)_2]NO_3{\cdot}HNO_3$ (2) has been synthesized. The crystal structure of this complex and the related complex $[Co(cyclam)(NH_3)_2]Cl_2BF_4{\cdot}2H_2O$ (1) have been determined. Crystal data for (1): M 451.04, monoclinic, space group $P2_1/c$ (No. 14), a 7.3927(10), b 13.3082(7), c 19.524(2) Å, β 97.625(14)°, V 1903.9(3) Å^3, F(000) 936, Z 4, D_c 1.574 g cm^{-3}, μ 1.225 cm^{-1}, Mo Kα (graphite monochromatized) λ 0.71073 Å, T 293(1) K. Crystal data for (2): M 571.33, triclinic, space group $P\bar{1}$ (No. 2), a 7.3988(14), b 8.5682(16), c 9.209(3) Å, α 89.02(2), β 76.64(3), γ 82.340(16)°, V 562.9(2) Å^3, F(000) 296, Z 1, D_c 1.685 g cm^{-3}, μ 0.854 cm^{-1}, Mo Kα (graphite monochromatized) λ 0.71073 Å, T 293(1) K. In both complexes the complex crystallizes in the *trans*-III form with the cobalt in the usual octahedral environment.

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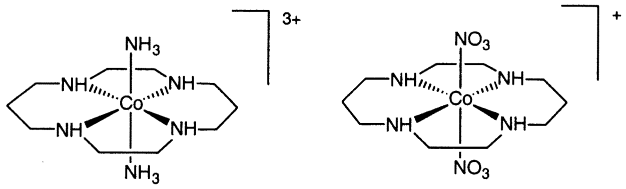
Introduction

We have been interested in using cobalt(III) complexes of cyclam (1,4,8,11-tetraazacyclotetradecane), appended with a variety of ancillary ligands, as acceptor groups of photochemically activated donor–acceptor complexes. As part of this work we have examined the preparation of cyclam complexes containing axially coordinated ammonia and primary or secondary amines. A preparation of the complex $[Co(cyclam)(NH_3)_2]^{3+}$ (1) (Fig. 1), in which liquid ammonia was used to replace the chloride ligands in $[Co(cyclam)Cl_2]^+$, has been reported previously.[1] In this method the complex is purified by the dissolution of the crude product in water followed by the addition of excess concentrated hydrochloric acid. In our hands, addition of HCl to $[Co(cyclam)(NH_3)_2]^{3+}$ (1) resulted in the reformation of the original green starting material; that is, $[Co(cyclam)Cl_2]^+$. We were, however, able to circumvent this problem by recrystallization of the crude product from aqueous $NaBF_4$. Under these circumstances the complex was isolated as the mixed salt $[Co(cyclam)(NH_3)_2]Cl_2BF_4$ (1), and this occurred even despite recrystallization in the presence of a large excess of $NaBF_4$. The presence of the BF_4^- ion is confirmed by the observation of the ν_3 stretch of the BF_4^- ion[2] in the infrared spectrum of $[Co(cyclam)(NH_3)_2]Cl_2BF_4{\cdot}2H_2O$ (1) at 1065 cm^{-1}.



$[Co(cyclam)(NH_3)_2]^{3+}$ (1) $[Co(cyclam)(NO_3)_2]^+$ (2)

Fig. 1. Cobalt(III) complexes derived from 1,4,8,11-tetraazacyclotetradecane: $[Co(cyclam)(NH_3)_2]^{3+}$ (1) and $[Co(cyclam)(NO_3)_2]^{3+}$ (2).

Results and Discussion

Our attempts to prepare cyclam complexes containing primary or secondary amines by amine ligand exchange with $[Co(cyclam)Cl_2]Cl$, or beginning from cobalt(II) salts, cyclam, and an amine followed by aerial oxidation were unsuccessful, and we failed to isolate solid products containing these amines. Generally these reactions yielded the aquahydroxo or dihydroxo cobalt(III) cyclam species. It has been reported that the NO_3^- ion functions as an excellent leaving group in the complex $[Cr(cyclam)(NO_3)_2]NO_3$, and that the coordinated nitrate is readily displaced by ligands such as NH_3, H_2O, Me_2SO, and dimethylformamide.[3] This observation indicated that the cobalt(III) analogue could be a useful starting material in our efforts to obtain cobalt(III)–cyclam compounds containing axially coordinated amine ligands. As a result, the complex $[Co(cyclam)(NO_3)_2]NO_3{\cdot}HNO_3$ (2) was prepared as a starting material. The synthetic method employed was similar to that used to prepare the

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chromium(III) counterpart, and involved reaction of the axial chloride ligands and chloride counter ion of [Co(cyclam)Cl_2]Cl with $AgNO_3$ to form AgCl. After removal of the resulting AgCl precipitate, the reaction mixture was concentrated in the presence of an excess of HNO_3. This resulted in the formation of dark purple needles of (2). The actual formulation of the complex was found by single-crystal X-ray diffraction to be [Co(cyclam)$(NO_3)_2$]NO_3·2HNO_3 (2). Loss of one of the nitric acid molecules is observed upon drying to leave the mono-solvate [Co(cyclam)$(NO_3)_2$]NO_3·HNO_3 (2) as determined by microanalysis. The presence of both coordinated and non-coordinated nitrate is confirmed by the infrared (IR) spectrum of the complex. The ν_2, ν_3 and ν_4 modes of vibration of the free NO_3^- ion are observed at 819, 1384 and 686 cm^{-1}, whilst the ν_1 and ν_2 vibrations of the ion singly coordinated to cobalt(III) are observed at 1265 and 998 cm^{-1}, as expected.[2,4]

Subsequent attempts, starting with [Co(cyclam)$(NO_3)_2$]-NO_3·HNO_3 (2), to prepare cyclam complexes containing primary or secondary amines were also unsuccessful. The preparations consisted of either dissolving or suspending (2) in the neat amine (butylamine or propylamine) or an aqueous solution of the amine. The resulting solutions/suspensions were either heated for a period of time or stirred at room temperature for prolonged periods. In a similar vein, suspension of (2) in the neat imine pyridine, followed by refluxing the mixture over 30 h (during which time the solid dissolved and a yellow solution formed) and solvent removal, also failed to yield a complex containing pyridine ligands as determined by ^1H nuclear magnetic resonance (NMR) spectroscopy.

The failure of primary or secondary amines to coordinate to the cobalt(III)–macrocycle unit may be due to steric hindrance from the amine protons of the cyclam ligand, which are situated close to the axial sites in these complexes.

Table 1. Selected bond lengths (Å) and angles (deg) for [Co(cyclam)$(NH_3)_2$]BF_4Cl_2 (1)

Bond length (Å)		Bond angle (deg)	
Co–N8	1.964(4)	N8–Co–N16	91.6(2)
Co–N16	1.974(4)	N8–Co–N1	179.0(3)
Co–N1	1.976(5)	N16–Co–N1	88.9(2)
Co–N4	1.978(5)	N8–Co–N4	93.9(3)
Co–N15	1.989(4)	N16–Co–N4	90.6(2)
Co–N11	1.989(5)	N1–Co–N4	86.8(3)
		N8–Co–N15	88.2(2)
		N16–Co–N15	179.8(2)
		N1–Co–N15	91.2(2)
		N4–Co–N15	89.5(2)
		N8–Co–N11	86.3(2)
		N16–Co–N11	89.8(2)
		N1–Co–N11	93.0(3)
		N4–Co–N11	179.6(3)
		N15–Co–N11	90.1(2)

Table 2. Selected bond lengths (Å) and angles (deg) for [Co(cyclam)$(NO_3)_2$]NO_3·2HNO_3 (2)

Bond length (Å)		Bond angle (deg)	
Co–O15^A	1.917(2)	O15^A–Co–O15	180.00(8)
Co–O15	1.917(2)	O15^A–Co–N1	85.22(8)
Co–N1	1.976(2)	O15–Co–N1	94.78(8)
Co–N1^A	1.976(2)	O15^A–Co–N1^A	94.78(8)
Co–N4	1.976(2)	O15–Co–N1^A	85.22(8)
Co–N4^A	1.976(2)	N1–Co–N1^A	180.0(1)
		O15^A–Co–N4	85.96(9)
		O15–Co–N4	94.04(9)
		N1–Co–N4	93.60(9)
		N1^A–Co–N4	86.40(9)
		O15^A–Co–N4^A	94.04(9)
		O15–Co–N4^A	85.96(9)
		N1–Co–N4^A	86.40(9)
		N1^A–Co–N4^A	93.60(9)
		N4–Co–N4^A	180.0(2)

^{A} Symmetry transformations used to generate equivalent atoms: –*x*, –*y*, –*z*.

Description of Crystal Structures

Selected bond lengths and angles for complexes [Co(cyclam)$(NH_3)_2$)]BF_4Cl_2 (1) and [Co(cyclam)$(NO_3)_2$)]-NO_3·2HNO_3 (2) are given in Tables 1 and 2. Diagrams of the cations are shown in Figures 2 and 3, respectively. In both of the structures, the cobalt atom is in an octahedral environment with the monodentate ligands in a trans coordination geometry. The octahedron defined by the ligands is slightly distorted due to the geometric restrictions imposed by the five- and six-membered chelate rings of the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane. The cobalt–nitrogen bond distances of the cyclam ligand vary between 1.94 and 2.02 Å for [Co(cyclam)$(NH_3)_2$]$(BF_4)Cl_2$·2H_2O (1). For [Co(cyclam)$(NO_3)_2$]NO_3·2HNO_3 (2) the Co–N bond distances are all equivalent, at 1.976 Å.

In both complexes the cyclam ligand chelates to the cobalt as the *trans*-III isomer. The bite angle for the five-membered ethylene bridges are all slightly less than 90°, varying from 86.3(2) to 86.8(3)°, whilst for the propylene bridge the bite angles are all greater than 90°, varying between 93.0(3) and 93.9(3)°, as reported for related cyclam complexes.[5,6] The five-membered rings are slightly twisted, whilst the atoms of the six-membered rings are in a chair conformation, and all bond lengths in the cyclam-ligand backbone are similar to those found previously for related cyclam complexes.[5,7] The cobalt atom lies in the least-squares mean plane defined by the cyclam-ligand backbone in both (2) and (1).

For (2), the cobalt ion is situated on the centre of inversion of the small triclinic cell containing only one cobalt complex per unit cell.

The structure of (1) reveals one BF_4^- and two chloride counter ions, consistent with the elemental analysis of this complex as the mixed salt. The axial ammine ligands display Co–N bond lengths that are within the range given above for the Co–N bond lengths of the macrocycle. The complex crystallizes with two water molecules in the lattice; these are lost upon exposure of the crystal to air. The crystal packing

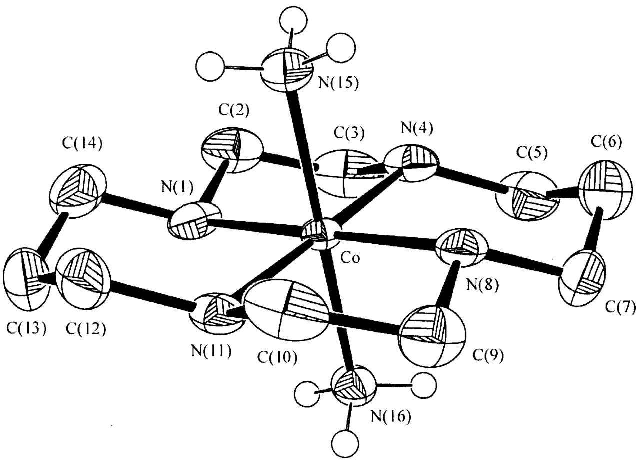

Fig. 2. Structure of the $[Co(cyclam)(NH_3)_2]^{3+}$ (1) cation. Displacement ellipsoids are at the 50% probability level. The hydrogen atoms of ammonia are included; all other hydrogen atoms have been omitted.

within the lattice is stabilized by strong hydrogen bonding between the axial ammine hydrogens and the fluorine atoms of the tetrafluoroborate anion and the chloride ions. The complexes are packed with the planes of the adjacent cyclam-ligand backbones parallel, forming channels in the solid. The space in between the channels is taken up by the anions that are hydrogen bonded to the ammine hydrogen atoms.

The complex $[Co(cyclam)(NO_3)_2]NO_3{\cdot}2HNO_3$ (2) contains nitrato axial ligands. The Co–O bond lengths, at 1.917 Å, are comparable to those found for other Co(III) complexes containing the nitrato ligand.[8] The Co–O bond is stabilized further by the formation of an intramolecular hydrogen bond between the non-chelating oxygen of the nitrato ligand, O17, and the amine hydrogens of the cyclam ligand. This contact approach is relatively long, with the O17–N1 and O17–N4 atoms approaching to within 2.969(3) and 3.003(3) Å of one another, respectively. The nitrogen atoms of the nitrato ligands also approach within hydrogen-bonding distance of the amine hydrogen atoms. As well as the intramolecular hydrogen bonding, hydrogen bonding between the nitrato anion and amine hydrogens occurs. There are no hydrogen bonding contacts between the cobalt complex and nitric acid molecule, which fills in channels throughout the structure. The crystal packing in the cell is similar to that observed for (1).

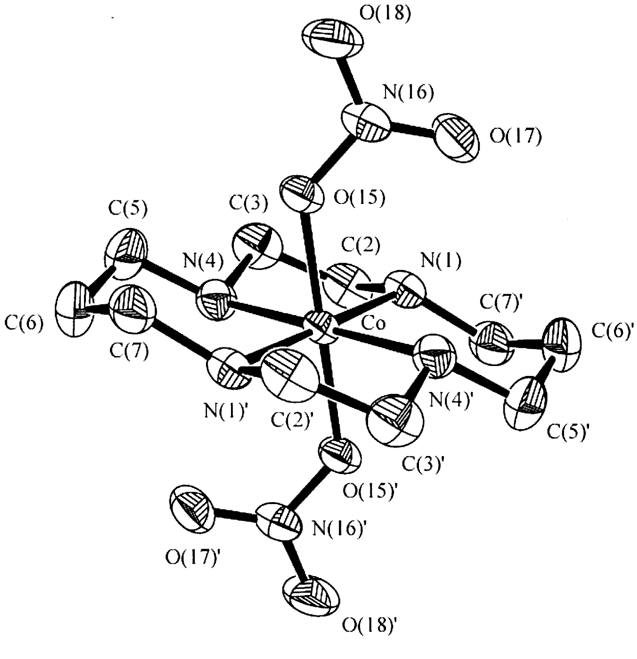

Fig. 3. Structure of the $[Co(cyclam)(NO_3)_2]^{3+}$ (2) cation. Displacement ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted.

Experimental Section

Synthesis

General Conditions, Reagents, and Instruments

The ligand 1,4,8,11-tetraazacyclotetradecane was used as received (Sigma). The complex $[Co(1,4,8,11\text{-tetraazacyclotetradecane})(NH_3)_2]Cl_2BF_4$ (1) was synthesized according to a modification of the literature method.[1] Ultraviolet–visible spectra were recorded on aqueous solutions using a Hewlett-Packard 8452A Diode Array Spectrophotometer. IR data were recorded using a Bio-Rad FTS 165 Fourier-transform IR spectrometer on a sample dispersed in a KBr disk. ^1H NMR and ^{13}C NMR spectra were recorded in aqueous solutions on a Varian Unity-300 spectrometer with D_2O as solvent. Chemical shifts (δ, positive downfield) are given in ppm and sodium trimethylsilylpropanesulfonate was used as an internal standard for ^1H NMR. ^1H chemical shift data are not given for exchangeable (amine) protons due to the variation between samples in position and intensity of these signals. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. All reagents used were of AR grade.

Bis(ammine)(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Dichloride Tetrafluoroborate Dihydrate, $[Co(cyclam)(NH_3)_2]Cl_2BF_4{\cdot}2H_2O$ (1)

In this case, *trans*-$[Co(1,4,8,11\text{-tetraazacyclotetradecane})Cl_2]BF_4$ (0.539 g, 1.29 mmol) (prepared by the recrystallization of *trans*-$[Co(1,4,8,11\text{-tetraazacyclotetradecane})Cl_2]^+$ from an aqueous solution containing an excess of $NaBF_4$) replaced *trans*-$[Co(1,4,8,11\text{-tetraazacyclotetradecane})Cl_2]Cl$ in the following modification of the literature synthesis.[1] Finely ground *trans*-$[Co(cyclam)Cl_2]BF_4$ (0.539 g, 1.29 mmol) was suspended and stirred in liquid ammonia (60 mL), whereupon the green solid was transformed into a light orange solid. The liquid ammonia was allowed to boil off. The resulting solid was dissolved in water (7 mL), filtered, and then $NaBF_4$ (0.403 g, 3.67 mmol) was added to the solution. Upon the addition of ethanol (4 mL) a fine orange precipitate formed. The reaction mixture was cooled to 4°C and then the product was collected, washed with ice-cold water (2 × 0.5 mL) and ethanol (2 × 2 mL) and dried at the pump to yield *$[Co(1,4,8,11\text{-tetraazacyclotetradecane})(NH_3)_2]Cl_2BF_4{\cdot}2H_2O$* (0.259 g, 0.53 mmol, 41%). Found: C, 25.0; H, 6.4; N, 17.1%. $C_{10}H_{30}BCl_2CoF_4N_6{\cdot}2H_2O$ requires C, 24.7; H, 7.0; N, 17.3%. Visible λ_{max}: 466 nm, ε_{max}: 43.0 L mol^{-1} cm^{-1}. ^1H NMR δ (D_2O) 1.86, dq, 2H, cyclam CH_2; 2.23, d, 2H, cyclam CH_2; 2.52, t, 4H, cyclam CH_2; 2.71, d, 4H, cyclam CH_2; 2.89, dd, 4H, cyclam CH_2; 3.12, d, 4H, cyclam CH_2.

Bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Nitrate HNO_3, $[Co(cyclam)(NO_3)_2]NO_3{\cdot}HNO_3$ (2)

Caution! The evaporation of solutions containing nitric acid may lead to the formation of products that are potentially explosive. Due care must be exercised in the preparation and handling of such solutions.

A solution of $AgNO_3$ (1.416 g, 8.34 mmol) and concentrated HNO_3 (1 mL) in water (10 mL) was added to a solution of [Co(1,4,8,11-tetraazacyclotetradecane)Cl_2]Cl (1.016 g, 2.78 mmol) in warm water (20 mL). A white precipitate of AgCl formed immediately. The suspension was stirred with heating at 95°C for 1 h, and then stirred for a further hour at room temperature. The AgCl precipitate was removed by filtration to give a dark purple solution to which concentrated HNO_3 (20 mL) was added. The solution was reduced in volume at 80°C to 10 mL, during which time dark purple crystals formed. The solid was collected, washed with ice-cold water and dried under vacuum at 80°C for 2 h to yield *[Co(1,4,8,11-tetraazacyclotetradecane)(NO$_3$)$_2$]-NO$_3$·HNO$_3$* (0.683 g, 1.34 mmol, 48%). Found: C, 23.7; H, 5.0; N, 22.4%. $C_{10}H_{24}CoN_7O_9{\cdot}HNO_3$ requires C, 23.6; H, 5.0; N, 22.0%. Visible λ_{max}: 572 nm, ε_{max}: 34.6 L mol^{-1} cm^{-1}. ^{1}H NMR δ (D_2O) 2.32, m, 4H, cyclam-CH_2; 2.71, m, 12H, cyclam-CH_2; 3.06, m, 4H, cyclam CH_2.

Crystallography

Crystal Data

[Co(cyclam)(NH$_3$)$_2$]Cl$_2$BF$_4$ (1). M 451.04, monoclinic, space group $P2_1/c$ (No. 14), a 7.3927(10), b 13.3082(7), c 19.524(2) Å, β 97.625(14)°, V 1903.9(3) Å^3, F(000) 936, Z 4, D_c 1.574 g cm^{-3}, μ 1.225 cm^{-1}, Mo Kα (graphite monochromatized) λ 0.71073 Å, T 293(1) K.

[Co(cyclam)(NO$_3$)$_2$]NO$_3$·2HNO$_3$ (2). M 571.33, triclinic, space group P(No. 2), a 7.3988(14), b 8.5682(16), c 9.209(3) Å, α 89.02(2), β 76.64(3), γ 82.340(16)°, V 562.9(2) Å^3, F(000) 296, Z 1, D_c 1.685 g cm^{-3}, μ 0.854 cm^{-1}, Mo Kα (graphite monochromatized) λ 0.71073 Å, T 293(1) K.

Data Collection

Single X-ray quality crystals of (1) were grown by the slow diffusion of ethanol into an aqueous solution of the complex. The data for (1) were collected from an orange prism of approximate dimensions 0.21 by 0.27 by 0.31 mm in a sealed capillary tube in the presence of mother liquor. Single X-ray quality crystals of (2) were grown by the slow evaporation of the reaction mixture and data were collected from a purple needle of approximate dimensions 0.16 by 0.16 by 0.26 mm in a sealed capillary tube in the presence of mother liquor.

Details of the data collection refer to [Co(cyclam)(NH_3)$_2$]Cl_2BF_4 (1). The corresponding details for [Co(cyclam)(NO_3)$_2$]$NO_3{\cdot}2HNO_3$ (2) are given in parentheses. Accurate unit cell parameters were calculated using a least-squares procedure from the setting angles of 25 reflections. Intensity data were collected on an Enraf–Nonius CAD4-MachS single-crystal X-ray diffractometer. The $\omega : 2\theta$ scan method and graphite monochromatized Mo Kα radiation, λ 0.71073 Å, were used. During collection three intensity control reflections were monitored every 9600 s of X-ray exposure time. These showed no deterioration in intensity for either complex. A total of 4178 (3170) reflections were measured, $2 \le 2\theta \le 25°$ ($2 \le 2\theta \le 27.5°$) of which 3341 (2575) were unique (R_{int} 0.0296 (0.0112)) and 1914 (2478) considered observed ($I \ge 2\sigma(I)$). Corrections were applied for Lorentz and polarization effects as well as for absorption, the corrections being evaluated by Gaussian integration.[9] The maximum and minimum transmission factors were 0.7998 and 0.6863 (0.8035 and 0.7550).

Both structures were solved using a combination of direct methods and difference synthesis[10] and were refined using a full-matrix least-squares procedure based on F^2.[11] For (1) the tetrafluoroborate anion was found to be disordered and was included in the refinement in two orientations constrained to geometrical estimates. For (2) the HNO_3 solvent molecules were found to be disordered, these were also included in the refinement in two orientations constrained to geometrical estimates. Hydrogen atoms were located from the difference map and were constrained to geometrical estimates. Final refinement was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms with isotropic displacement parameters applied to hydrogen atoms. A weighting scheme of type $[\sigma^2(F_o^{\,2}) + (aP)^2 + bP]^{-1}$, where $a = 0.0586$ and $b = 1.9604$ (0.0783 and 0.4647), was used where $P = (\max(F_o^{\,2},0) + 2F_c^{\,2})/3$. At convergence, $R_1(I \ge 2\sigma(I))$ was 0.0446 (0.0451), wR_2(all data) 0.1313 (0.1279), and S 1.025 (1.077), where $R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma(w(F_o^{\,2} - F_c^{\,2})^2)/\Sigma w(F_o^{\,2})^2)^{1/2}$. For (1) the final difference map showed a number of electron density peaks (maximum and minimum peak height 0.475 and –0.391 e Å^{-3}) around the fluorine atoms of the disordered tetrafluoroborate anion. For (2) the maximum and minimum peak heights were 0.640 and –0.843 e Å^{-3}, close to the disordered nitric acid molecules.

The atomic scattering factors were those incorporated in the SHELXL-97 program system.[11] Calculations were carried out on a Vaxstation 4000VLC computer system. The Figures of the cations were prepared from the output of ORTEP3 for Windows.[12] Final atomic coordinates and isotropic displacement parameters as well as selected bond lengths and angles for complexes (1) and (2) are given in Tables 1 and 2 respectively. Hydrogen atom coordinates, complete geometry, displacement parameters and a listing of the observed and calculated structure factors have been deposited. Copies are available, until December 2007, from *Australian Journal of Chemistry—an International Journal for Chemical Science* (website: http://www.publish.csiro.au/journals/ajc/AccessMat.cfm).

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References

[1] B. Bosnich, C. K. Poon, M. L. Tobe, *Inorg. Chem.* **1965**, *4(8)*, 1102.

[2] K. Nakamoto, (Ed.) *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry* 5th Edn **1997**, Vol. 1 (John Wiley & Sons: New York).

[3] N. A. P. Kane-Maguire, K. C. Wallace, D. B. Miller, *Inorg. Chem.* **1985**, *24*, 597.

[4] K. Nakamoto, (Ed.) *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry* 5th Edn **1997**, Vol. 2 (John Wiley & Sons: New York).

[5] M. E. Sosa-Torres, R. A. Toscano, *Acta. Crystallogr. Sect. C: Cryst. Struct. Commun.* **1997**, *53*, 1585.

[6] J. Burgess, J. Fawcett, R. I. Haines, K. Singh, D. R. Russell, *Trans. Met. Chem.* **1999**, *24*, 355.

[7] S. P. Sovilj, G. Vuckovic, K. Babic, N. Matsumoto, M. Avramov-Ivic, V. M. Jovanovic, *J. Coord. Chem.* **1994**, *31*, 167.

[8] E. Yasaki, I. Oonishi, H. Kawaguchi, S. Kawaguchi, Y. Komiyama, *Bull. Chem. Soc. Jpn* **1970**, *43*, 1354.

[9] G. M. Sheldrick, *SHELXS76 Program for Crystal Structure Solution* **1976** (Cambridge: England).

[10] G. M. Sheldrick, *Acta. Crystallogr., Sect A: Fundam. Crystallogr.* **1990**, *46*, 467.

[11] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures* **1997** (University of Göttingen: Germany).

[12] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.