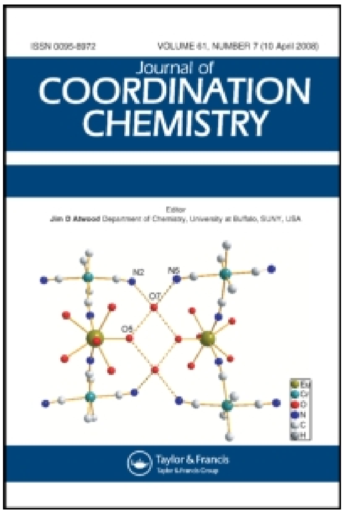

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THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO DERIVATIVES OF WERNER'S HEXOL CLUSTER CATION: $[Co\{(OH)_2Co(NH_3)_4\}_3](NO_3)_5(OH)\cdot 4H_2O$(I) AND $[Co\{(OH)_2Co(NH_3)_4\}_3](NO_3)_6\cdot 2H_2O$(II)

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THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO DERIVATIVES OF WERNER'S HEXOL CLUSTER CATION: $[Co\{(OH)_2Co(NH_3)_4\}_3](NO_3)_5(OH)\cdot 4H_2O$(I) AND $[Co\{(OH)_2Co(NH_3)_4\}_3](NO_3)_6\cdot 2H_2O$(II)*

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Crystals of compound (I) and (II) are black in reflected light and brown–black in transmitted light. The ^{1}H-nmr of the cations of (I), recorded in D^6-DMSO, show peaks, relative to the ^{1}H of D^6-DMSO, at + 0.46 ppm(rel. int. = 3); +0.85 ppm(rel. int. = 1.2); +1.80 ppm (rel. int. = 3); and −4.18 ppm(rel. int. = 1). The magnetic susceptibility of (I) is C'_m (293.18 K) = 588.45×10^{-6} c.g.s. units, which corresponds to a $m_{eff} = 0.295$ B.M. per Co ion; however, the small shifts and sharp ^{1}H-nmr lines in the DMSO spectrum preclude the presence of paramagnetic clusters. Cyclic voltametry of the cation present in (I) shows highly distorted, irreversible, oxidation and reduction waves which indicate the lack of stability of any oxidized or reduced form – a fact which accords with the sharp lines of the NMR spectra; *e.g.*, no stable paramagnetic species are present in (I).

Compound (I), $M.W. = 941.24$, crystallizes in $P2_1/n$ (No. 14), with cell constants $a = 11.789(2)$, $b = 13.855(2)$, $c = 21.534(3)$ Å, $\beta = 91.94(1)°$; $V = 3515.44$ Å^3, d (meas; $z = 4$) = 1.778 gm-cm^{-3}. A total of 4705 data were collected in the range $4° \leq 2\Theta \leq 50°$. They were corrected for absorption ($\mu = 19.562$ cm^{-1}; rel. trans. coeff. range = 0.8642 to 0.9997); of these, 2623 were unique and had $I \geq 3\sigma(I)$. The structure was solved by direct methods, none of the hydrogens of the amine ligands were found experimentally at sensible positions; thus, they were left out. Refinement of the heavy atoms (anisotropic) led to final residuals of $R(F) = 0.0637$ and 0.0771.

Compound (II), $M.W. = 950.20$, crystallizes in space group P1 (bar; No. 2), with cell constants $a = 12.858(3)$, $b = 12.475(2)$, $c = 12.114(2)$ Å, $\alpha = 96.63(1)$, $\beta = 91.94(1)$ and $\gamma = 61.71(2)°$; $V = 1615.68$ Å^3, d(meas; $z = 2$) = 1.953 gm-cm^{-3}. A total of 5657 data were collected in the range $4° \leq 2\Theta \leq 50°$. They were corrected for absorption ($\mu = 21.301$ cm^{-1}; rel. trans. coeff. range = 0.7372 to 0.9998); of these, 4456 were unique and had $I \geq 3\sigma(I)$. The structure was

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*In Memoriam Alfred Werner: On the 109th Anniversary of the Presentation of his Habilitationschrift, October, 1891.

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solved by direct methods, the majority of the hydrogens of the amine ligands were found experimentally at sensible positions, the rest were calculated at idealized positions (N—H = 0.95 Å). The hydrogens of the OH ligands were located experimentally in a final difference Fourier map. Refinement of the heavy atoms (anisotropic) with fixed hydrogens ($B = 5.00$ Å^2) led to final residuals of $R(F) = 0.0348$ and 0.0440.

Precisely as visualized by Werner, the hexol cations consist of a central Co(III) cation surrounded by three $[Co(NH_3)_4(OH)_2]^{1+}$ ligands. In (I), the O—Co1—O angles are acute (av. value = 82.97°), as expected from the electrostatic repulsion of the Co(III) central cation and the monopositive ligands surrounding it. Consequently, the Co....Co distances are long (2.896, 2.888 and 2.889 Å; on average, 2.891 Å) and the the av. Co—O—Co angles are 97.43°. The remaining portions of the cation and anions are as expected from standard values; *i.e.*, Co—O = 1.90 - 1.95 and Co—N = 1.95 - 2.00 Å. In (II), the Co1—O—Co angles are also obtuse (av. value = 97.87°), as expected from the electrostatic repulsion of the Co(III) central cation, and the Co...Co distances are equally long (2.881, 2.876 and 2.874 Å; on average, 2.877 Å).

Keywords: DMSO spectrum; Heavy atoms; Oxidation; Werner method

INTRODUCTION

In 1890 Alfred Werner finished his doctoral dissertation studies, "Über räumlische Anordnung der Atome in stickstoffhaltigen Molekülen", which in that year were presented to the faculty of the Universität Zürich. "On the 16th of October, 1891, from the Hotel Pfauen, where he now resided, Werner submitted his Habilitationschrift to the Hohe Schweizerische Schulrat and petitioned for the *venia docendi* in Chemistry at the Polyteck-nicum" [1a]. Upon his appointment as Privat-Dozent, Werner began a series of studies of metal complexes which provided the basis for his first major paper in this field: "Beitrag zur Konstitution anorganischer Verbindungen" published (1893) [2] in the third volume of the recently founded *Zeitschrift für Anorganische Chemie*, where "it aroused instantaneous interest – and criticism" [1b].

It appears that the first cobalt amine species recognized as such were the $[Co(NH_3)_6]^{3+}$ cations described by Tassaert [3] (see also Ref. [1c]). By 1878, Jorgensen was preparing [4] large numbers of these intriguingly colored, but bewildering compounds, which Werner undertook to study early in his career. Among the myriad compounds prepared in his laboratory, a class of cobalt amines stands high as a mark of his experimental and theoretical abilities – the cluster cations of composition $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, for these substances provided the final proof of his theory of octahedral co-ordination, as evidenced by optical activity of species containing bidentate ligands. Since he died at a relatively early age, it was Werner's misfortune to miss the satisfaction of seeing this last building block of his superb scientific edifice set in place.

On our part, it was our good fortune to prepare, in time for the 109th centennial of the presentation of his Habilitationschrift, two crystalline derivatives of the tetra-nuclear cations, both of which were suitable for X-ray diffraction work. The results of these studies are dedicated to Alfred Werner as a tribute to his genius.

EXPERIMENTAL

Syntheses

Compound (I): $[Co(NH_3)_4(NO_2)_2]NO_3$ was prepared according to a literature procedure [5]. The red-brown salt was dissolved in water previously heated to 80°C, whereupon the solution turned brown–black. After some minutes, the solution was allowed to slowly cool to room temperature, filtered, and the filtrate allowed to sit overnight in a covered beaker. A small number of well-formed, shiny black crystals were filtered and used for the physical measurements described below. One, a fairly uniformly shaped crystal, was used in the X-ray diffraction measurements.

Compound(II): $[Co(NH_3)_4CO_3]\ NO_3{\cdot}1/2H_2O$ was prepared by a known method [6]. In the course of preparing a series of $[Co(NH_3)_4(\text{amino-acidato})]^{2+}$ derivatives, $[Co(NH_3)_4CO_3]\ NO_3{\cdot}1/2H_2O$ was dissolved in water and an equimolar amount of $NaNO_3$ and of racemic *p*-tyrosine were added in order to prepare $[Co(NH_3)_4(p\text{-tyrosinato})]\ (NO_3)_2$. After sitting for about 21 days in a refrigerator (*ca.* 5°C), the pink solution deposited, first, a small number of shiny black crystals resembling those obtained in the preparation of (I). One of them was selected for X-ray diffraction work.

Elemental Analyses Satisfactory elemental analyses for both compounds were reported to us [7]. For (I), Theory: $H = 5.46$, $N = 25.30$, $H_2O = 7.67$; Exp: $H = 5.28$, $N = 25.16$, $H_2O = 8.34$. For (II): Theory: $H = 4.88$, $N = 26.53$; Exp: $H = 4.98$, $N = 26.36$, $H_2O = 8.34$. See DTA and DSC.

DTA and DSC Analyses Since compound (I) contains both waters of crystallization and OH^- anions, we subjected the compound to both differential thermal analyses and differential scanning calorimetry scans. These studies [8] indicate that there are two sequential losses of weight in the temperature range of 40 to 125°C, each loss corresponding to two moles of water per mole of the compound. The onset of chemical decomposition occurs at about 190°C [8].

Mass Spectra These were recorded with a VG-70 instrument and the results were very revealing regarding ion associations. For example in compound (I) one observes a mass peak at 796 which probably corresponds to the cluster (compound $-2NO_3$—H_2O); also, there is a mass peak at 731 corresponding to the mass of the cluster (compound $-3NO_3$—H_2O), *etc*.... Similar results were obtained with compound (II). Such results indicate that these (cation + anion(s) + water(s)) clusters must have reasonably large lifetimes and that the bonding holding them together (hydrogen bonds) is fairly robust.

Cyclic Voltametry Performed in DMSO, using $[(n\text{-butyl})_4N]ClO_4$ as the supporting electrolyte. The results were distorted oxidation and reduction waves which suggest serious, rapid decomposition of the clusters (see Acknowledgements).

^{1}H-nmr Spectra Recorded in D^6-DMSO. The proton NMR lines were referenced to the ^{1}H of the D^6-DMSO, which occurred at 2.49 ppm with respect to TMS. The spectrum consists of four very sharp lines located +0.46, +0.85, +1.80 and −4.18 ppm (from the DMSO peak) with approximate relative intensity ratios of 3:1.2:3:1. We attribute the lines with intensity 3 to the protons of the axial and equatorial amines. The peak at 0.85 ppm (intensity 1.2) to the waters of crystallization, which, no doubt are exchanging with the OH^- and, that at −4.18 ppm, to the OH ligand protons.

Magnetic Susceptibility of (I) Measured at 293.18°K using a Faraday Cahn Balance Model 6600-1 [9]. $C'_m = 588.45 \times 10^{-6}$ c.g.s. units, which corresponds to a $\mu_{\text{eff}} = 1.18$ B.M. per formula weight, or 0.295 B.M. per Co ion.

X-Ray Diffraction Analyses A crystal of (I) was mounted on an Enraf-Nonius CAD4 diffractometer and centered according to standard procedures [10, 11]. The Niggli matrix [12] indicated the cell was monoclinic, primitive. Systematic absences revealed the space group to be $P2_1/n$ (No. 14). The same procedure was used for the alignment and indexing data of compound (II), which was found to crystallize in the triclinic space group P1 (bar; No. 2).

Since in (II) the cations and nitrate anions (a) are in a ratio of 1 : 6, and (b) both have three-fold axes of symmetry, it would not have been unusual for this substance to crystallize in a trigonal, hexagonal or cubic space group, as was the case with the rhombohedral (or trigonal), compound of composition

$[Co\{(OH)_2Co(NH_3)_4\}_3]Cl_6 \cdot 8H_2O$(III), whose structural analysis was impossible to complete due to disorder [13]. We have recently verified [14] the reported results for the chloride salt [13] and that is why we selected to work with nitrate compensating anions.

The Niggli matrix for the cell describing compound (II) is

$$\begin{matrix} 150.86 & 155.62 & 146.75 \\ -21.18 & -17.18 & 72.62 \end{matrix}$$

the values of whose components somewhat resemble in magnitude those of a C-centered, monoclinic space group [12]. However, for a triclinic cell in which the symmetrical Niggli matrix components are $S_{11} \neq S_{22} \neq S_{33}$, the unsymmetrical components have to be all positive or all negative if one is to find a valid transformation to a higher symmetry cell [12]. Moreover, application of the relevant transformation matrix [12] results in a "C-centered monoclinic" cell with $a = 21.254(3)$, $b = 12.698(4)$, $c = 12.114(2)$ Å, $\alpha = 88.51°$, $\beta = 98.57°$ and $\gamma = 91.01°$. The deviations of α, β and γ from 90.0° are much too large for our diffractometer, whose alignment was checked against the Enraf–Nonius standard crystal. Thus, the space group was assigned as P1 (bar; No. 2). Refinement justifies this choice.

For both compounds, the data were collected using standard procedures [10, 11], corrected for Lorentz-polarization effects and for absorption (Psiscans [9, 10]). Both structures were solved using direct methods [10, 11]; for the refinement, the scattering curves of Cromer and Waber [15] were used. Details of data collection and refinement are summarized in Tables I and II. Final values of the discrepancy indices are (I): $R(F) = 0.0637$ and $R_w(F) = 0.0771$; while for (II): $R(F) = 0.0348$ and $R_w(F) = 0.0440$. Final positional parameters for (I) and (II), respectively, are listed in Tables III and IV. Only isotropic-equivalent thermal parameters are given for each compound in the manuscript. No sensibly placed hydrogen atoms were found in the case of (I); thus, the coordinates (Tab. III) contain only heavy atoms. In the case of (II), only the coordinates for the heavy atoms are listed in the text. However, a complete table of positional parameters (including hydrogens) is submitted as Supplementary Material (see below).

The structures of cations (I) and (II) are displayed in Figures 1 and 2. Packing diagrams are ignored as being quite complex and un-informative. However, since we had well-placed hydrogens in the case of (II), hydrogen bonds between the various components of the molecule are shown in

TABLE I Summary of data collection and processing parameters for $[Co\{(OH)_2Co(NH_3)_4\}_3](NO_3)_5(OH)\cdot 4H_2O(I)$

Space Group	$P2_1/n$(No. 14)
Cell Constants	$a = 11.789$ (2) Å
	$b = 13.855(2)$
	$c = 21.534(3)$
	$\beta = 91.94(1)°$
Cell Volume	$V = 3515.44$ Å^3
Molecular Formula	$Co_4O_{26}N_{17}H_{51}$
Molecular Weight	941.24 g-mole^{1}
Density (calc; z = 4 mol/cell)	1.778 g-cm^{-3}
Radiation Employed	MoKα ($\lambda = 0.71073$Å)
Absorption Coefficient	$\mu = 19.562$ cm^{-1}
Relative Transmission Coefficients	0. 8642 to 0. 9997
Data Collection Range	$4° \leq 2\Theta \leq 50°$
Scan Width	$\Delta\Theta = 0.90 + 0.35\tan\Theta$
Total Data Collected	4705
Data Used In Refinement*	2623
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0637
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]\|^{1/2}$	0.0771
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 2082 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, symmetry related, standards or did not meet the criterion that $I \geq 3\sigma(I)$.

TABLE II Summary of data collection and processing parameters for $[Co\{(OH)_2Co(NH_3)_4\}_3](NO_3)_6\cdot 2H_2O(II)$

Space Group	P1 (bar; No. 2)
Cell Constants	$a = 12.858$ (3) Å
	$b = 12.475(2)$
	$c = 12.114(2)$
	$\alpha = 98.06(1)°$
	$\beta = 96.63(2)$
	$\gamma = 61.71(2)$
Cell Volume	$V = 1615.68$Å^3
Molecular Formula	$Co_4O_{26}N_{18}H_{46}$
Molecular Weight	950.20 g-mole^{-1}
Density (calc; z = 2 mol/cell)	1.953 g-cm^{-3}
Radiation Employed	MoKα ($\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 21.301$ cm^{-1}
Relative Transmission Coefficients	0.7372 to 0.9999
Data Collection Range	$4° \leq 2\Theta \leq 50°$
Scan Width	$\Delta\Theta = 0.90 + 0.35\tan\Theta$
Total Data Collected	5657
Data Used In Refinement*	4456
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0348
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]\|^{1/2}$	0.0440
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 1201 data that were redundant, collected to obtain reflections suitable for the absorption correction, standards or did not meet the criterion that $I \geq 3\sigma(I)$.

TABLE III Positional parameters and their estimated standard deviations for I

Atom	*x*	*y*	*z*	B(Å^2)
Co1	0.4319(2)	0.2473(2)	0.64859(9)	1.86(4)
Co2	0.1970(2)	0.2631(2)	0.6800(1)	2.49(5)
Co3	0.6074(2)	0.2259(2)	0.7436(1)	2.50(5)
Co4	0.4928(2)	0.2549(2)	0.52058(9)	2.14(4)
O1	0.3246(8)	0.1770(7)	0.6940(4)	2.1(2)
O2	0.3063(8)	0.3342(7)	0.6365(4)	2.3(2)
O3	0.4815(8)	0.3137(7)	0.7228(4)	2.6(2)
O4	0.5525(7)	0.1607(7)	0.6695(4)	2.0(2)
O5	0.3930(8)	0.1850(7)	0.5725(4)	2.1(2)
O6	0.5346(8)	0.3149(7)	0.5976(4)	2.2(2)
O7	0.498(1)	0.4889(8)	0.3997(5)	4.1(3)
O8	0.429(1)	0.5021(8)	0.3068(5)	4.6(3)
O9	0.441(1)	0.3651(8)	0.3512(6)	4.8(3)
O10	−0.141(1)	0.476(1)	0.6446(6)	5.7(4)
O11	−0.189(1)	0.598(1)	0.6002(6)	8.3(5)
O12	−0.222(1)	0.468(1)	0.5577(8)	10.1(5)
O13	0.4897(9)	−0.0350(8)	0.7175(6)	4.3(3)
O14	0.575(1)	−0.1725(8)	0.7184(6)	5.1(3)
O15	0.659(1)	−0.049(1)	0.6856(7)	7.2(4)
O16	0.5839(9)	0.0105(8)	0.4234(6)	4.7(3)
O17	0.733(1)	0.0011(7)	0.3657(6)	4.1(3)
O18	0.683(1)	0.1364(8)	0.4002(6)	5.3(3)
O19	0.213(1)	0.0238(8)	0.8066(6)	5.2(3)
O20	0.303(1)	0.039(1)	0.8963(7)	7.9(5)
O21	0.233(1)	0.1629(8)	0.8508(6)	5.1(3)
O22	0.682(1)	0.374(3)	0.9548(6)	20(1)
N1	0.246(1)	0.329(1)	0.7573(6)	3.4(3)
N2	0.093(1)	0.179(1)	0.7259(6)	3.1(3)
N3	0.080(1)	0.362(1)	0.6635(6)	3.4(3)
N4	0.155(1)	0.199(1)	0.6014(6)	3.4(3)
N5	0.710(1)	0.2984(9)	0.6912(6)	2.8(3)
N6	0.728(1)	0.132(1)	0.7573(6)	3.5(3)
N7	0.654(1)	0.299(1)	0.8174(7)	4.4(4)
N8	0.497(1)	0.1565(9)	0.7950(6)	2.7(3)
N9	0.371(1)	0.351(1)	0.5059(6)	3.3(3)
N10	0.444(1)	0.189(1)	0.4431(6)	3.5(3)
N11	0.602(1)	0.330(1)	0.4750(6)	3.1(3)
N12	0.611(1)	0.1572(9)	0.5404(6)	3.0(3)
N13	0.455(1)	0.4509(9)	0.3520(6)	3.0(3)
N14	−0.183(1)	0.509(1)	0.6000(8)	5.8(5)
N15	0.574(1)	−0.085(1)	0.7061(7)	3.9(4)
N16	0.663(1)	0.0483(9)	0.3974(6)	3.8(3)
N17	0.250(1)	0.077(1)	0.8497(7)	4.2(4)
OW1	−0.112(1)	0.140(1)	0.6379(8)	9.2 (5)*
OW2	0.067(2)	0.380(2)	0.522(1)	7.7(6)*
OW3	0.841(2)	0.282(2)	0.548(1)	8.7(7)*
OW4	0.431(2)	0.307(2)	0.896(1)	10.0(8)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * [*a*2**B*(1,1) + *b*2 * *B*(2,2) + *c*2 * *B*(3,3) + *ab*(cos gamma) * *B*(1,2) + *ac*(cos beta) * *B*(1,3) + *bc*(cos alpha) * *B*(2,3)].

Figure 3. The final distances and angles and hydrogen contacts (for (II) only; see Discussion) are presented in Tables V and VI, respectively, for compounds (I) and (II).

TABLE IV Positional parameters and estimated standard deviations for II

Atom	*x*	*y*	*z*	*B* ($Å^2$)
Co1	0.32510(4)	0.31791(4)	0.24093(4)	1.49(1)
Co2	0.25127(5)	0.13113(4)	0.25175(5)	1.63(1)
Co3	0.13610(5)	0.56933(5)	0.23714(5)	1.79(1)
Co4	0.58272(5)	0.25614(5)	0.23392(5)	1.77(1)
O1	0.2278(2)	0.2846(2)	0.3287(2)	1.84(6)
O2	0.3517(2)	0.1634(2)	0.1647(2)	1.76(6)
O3	0.2862(2)	0.4734(2)	0.3222(2)	1.90(6)
O4	0.1784(2)	0.4122(2)	0.1524(2)	1.94(6)
O5	0.4767(2)	0.2379(2)	0.3274(2)	1.90(6)
O6	0.4292(2)	0.3365(2)	0.1480(2)	1.90(6)
N1	0.1032(3)	0.2232(3)	0.1568(3)	2.32(8)
N2	0.1485(3)	0.1083(3)	0.3478(3)	2.43(8)
N3	0.2822(3)	−0.0242(3)	0.1647(3)	2.57(9)
N4	0.3994(3)	0.0470(3)	0.3494(3)	2.35(8)
N5	0.0384(3)	0.5315(3)	0.3249(3)	2.33(8)
N6	−0.0093(3)	0.6574(3)	0.1403(3)	2.79(9)
N7	0.1031(3)	0.7166(3)	0.3361(3)	2.84(9)
N8	0.2378(3)	0.6031(3)	0.1482(3)	2.73(9)
N9	0.6156(3)	0.0938(3)	0.1642(3)	2.35(8)
N10	0.7276(3)	0.1825(3)	0.3345(3)	2.68(9)
N11	0.6810(3)	0.2684(3)	0.1251(3)	2.83(9)
N12	0.5463(3)	0.4203(3)	0.3045(3)	2.76(9)
N13	0.9678(3)	−0.0373(3)	0.1156(3)	2.97(9)
O7	0.8776(3)	−0.0318(4)	0.0571(3)	5.4(1)
O8	1.0647(4)	−0.1310(4)	0.1182(5)	7.8(2)
O9	0.9577(4)	0.0574(3)	0.1725(4)	5.8(1)
N14	0.1351(3)	0.6324(3)	0.6090(3)	2.60(9)
O10	0.1340(3)	0.6822(3)	0.7055(3)	3.86(9)
O11	0.0414(3)	0.6263(3)	0.5671(3)	4.25(9)
O12	0.2283(3)	0.5925(3)	0.5542(3)	4.4(1)
N15	0.3843(3)	0.1738(3)	−0.1084(3)	2.69(9)
O13	0.3931(3)	0.1410(3)	−0.2091(3)	4.0(1)
O14	0.2873(3)	0.2063(4)	−0.0607(3)	4.5(1)
O15	0.4758(3)	0.1745(4)	−0.0516(3)	4.7(1)
N16	−0.2097(3)	0.5181(3)	0.1317(4)	3.5(1)
O16	−0.1172(3)	0.4868(3)	0.0767(3)	4.9(1)
O17	−0.2899(3)	0.4869(4)	0.0917(4)	6.1(1)
O18	−0.2210(3)	0.5765(3)	0.2234(3)	4.9(1)
N17	0.6240(4)	0.2395(4)	0.6128(4)	4.3(1)
O19	0.5839(4)	0.3140(4)	0.5450(3)	6.2(1)
O20	0.7282(4)	0.1728(5)	0.6318(7)	12.0(2)
O21	0.5538(6)	0.2295(6)	0.6676(6)	14.3(3)
N18	−0.2067(4)	0.8899(3)	0.3727(3)	3.3(1)
O22	−0.3009(3)	0.9719(3)	0.4173(3)	4.3(1)
O23	−0.1603(3)	0.9113(3)	0.2976(3)	4.4(1)
O24	−0.1559(3)	0.7856(3)	0.4049(3)	4.6(1)
OW1	0.4625(4)	0.6275(4)	0.1106(5)	8.7(2)
OW2	0.3290(4)	0.2866(4)	0.5427(3)	7.3(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * [*a*2 * *B*(1,1) + *b*2 * *B*(2,2) + *c*2 * *B*(3,3) + *ab*(cos gamma) * *B*(1,2) + *ac*(cos beta) * *B*(1,3) + *bc*(cos alpha) * *B*(2,3)].

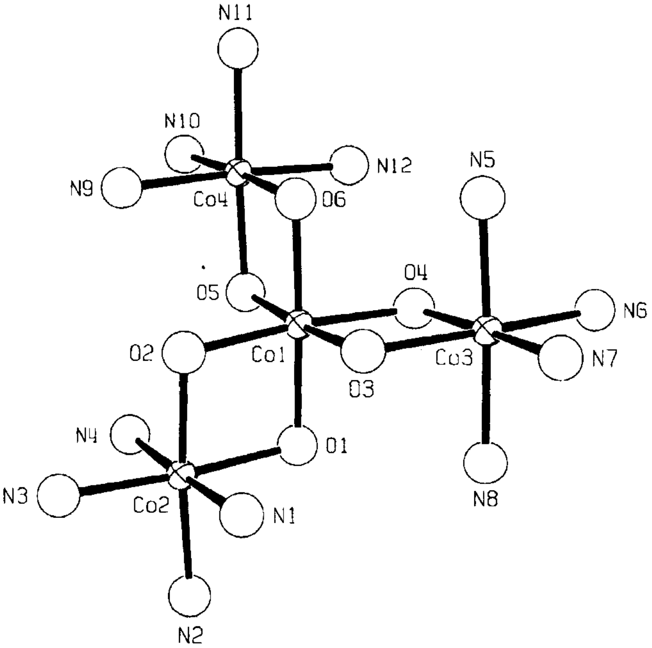


FIGURE 1 A labelled representation of the stereochemistry of the cation of (I).

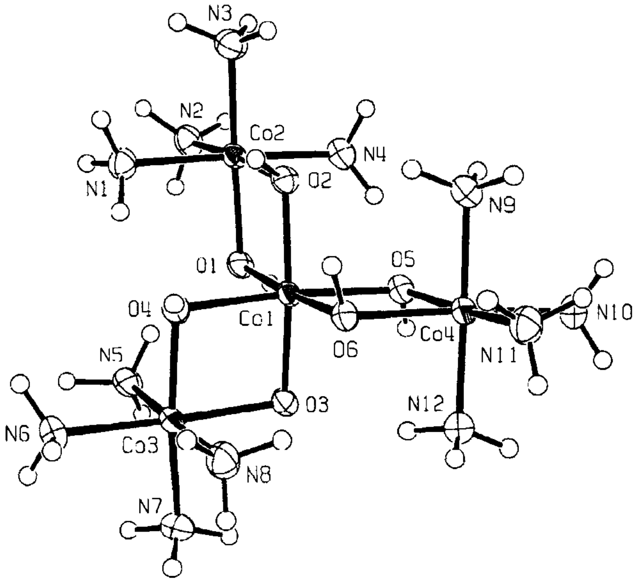


FIGURE 2 A labelled representation of the stereochemistry of the cation (II). The heavy atoms of the cation are represented with their anisotropic thermal parameters using 30% probability ellipsoids in order to avoid overlap of atoms and of labels.

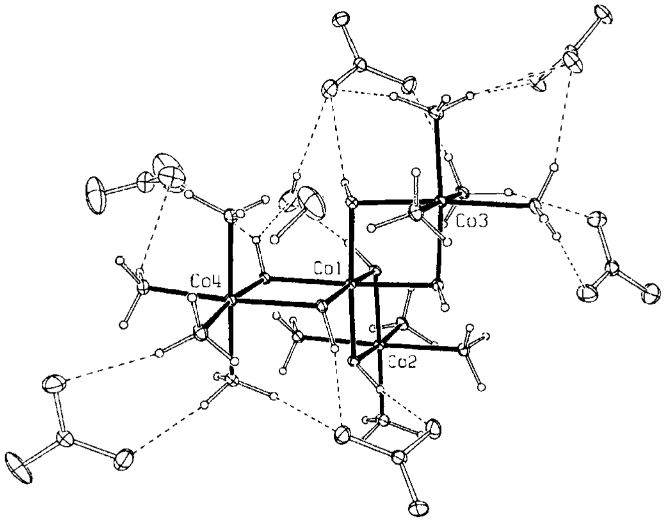


FIGURE 3 The cation, anions and waters held together in (**II**) by relatively strong hydrogen bonds. Those shown do not exceed 2.30 Å in length. For a more detailed description of the hydrogen bonding scheme, see Table VI(C).

TABLE V Bond distances and angles for I

*Atom*1	*Atom*2	*Distance*	*Atom*1	*Atom*2	*Distance*
(A) Bond distances in angstroms					
Cation					
Co1	O1	1.895(3)	Co1	O2	1.920(3)
Co1	O3	1.919(3)	Co1	O4	1.903(3)
Co1	O5	1.894(3)	Co1	O6	1.908(3)
Co2	O1	1.936(3)	Co2	O2	1.895(3)
Co2	N1	1.968(5)	Co2	N2	1.974(4)
Co2	N3	1.961(4)	Co2	N4	1.957(4)
Co3	O3	1.960(3)	Co3	O4	1.926(3)
Co3	N5	1.956(4)	Co3	N6	1.940(4)
Co3	N7	1.951(5)	Co3	N8	1.987(4)
Co4	O5	1.913(3)	Co4	O6	1.905(3)
Co4	N9	1.976(4)	Co4	N10	1.974(4)
Co4	N11	1.953(4)	Co4	N12	1.975(4)
Anions					
O7	N13	1.245(5)	O8	N13	1.233(5)
O9	N13	1.201(5)	O10	N14	1.164(7)
O11	N14	1.228(7)	O12	N14	1.160(7)
O13	N15	1.245(6)	O14	N15	1.241(6)
O15	N15	1.213(6)	O16	N16	1.226(6)
O17	N16	1.266(6)	O18	N16	1.244(6)
O19	N17	1.249(6)	O20	N17	1.272(6)
O21	N17	1.213(6)			

TABLE V (Continued)

*Atom*1	*Atom*2	*Atom*3	*Angle*	*Atom*1	*Atom*2	*Atom*3	*Angle*
(B) Bond angles in degrees							
Cation							
O1	Co1	O2	82.4(1)	O1	Co1	O3	90.4(2)
O1	Co1	O4	93.4(1)	O1	Co1	O5	93.8(2)
O1	Co1	O6	175.9(1)	O2	Co1	O3	91.4(1)
O2	Co1	O4	174.0(1)	O2	Co1	O5	90.3(1)
O2	Co1	O6	96.6(1)	O3	Co1	O4	84.3(1)
O3	Co1	O5	175.7(2)	O3	Co1	O6	93.6(1)
O4	Co1	O5	94.3(1)	O4	Co1	O6	87.8(1)
O5	Co1	O6	82.2(1)	O1	Co2	O2	81.9(1)
O1	Co2	N1	87.3(2)	O1	Co2	N2	92.9(2)
O1	Co2	N3	173.5(2)	O1	Co2	N4	91.5(2)
O2	Co2	N1	89.6(2)	O2	Co2	N2	174.8(2)
O2	Co2	N3	91.9(2)	O2	Co2	N4	87.9(2)
N1	Co2	N2	91.0(2)	N1	Co2	N3	90.6(2)
N1	Co2	N4	177.3(2)	N2	Co2	N3	93.3(2)
N2	Co2	N4	91.5(2)	N3	Co2	N4	90.3(2)
O3	Co3	O4	82.6(1)	O3	Co3	N5	91.5(2)
O3	Co3	N6	174.6(2)	O3	Co3	N7	92.9(2)
O3	Co3	N8	85.5(2)	O4	Co3	N5	87.7(2)
O4	Co3	N6	92.0(2)	O4	Co3	N7	175.5(2)
O4	Co3	N8	91.5(2)	N5	Co3	N6	88.3(2)
N5	Co3	N7	92.3(2)	N5	Co3	N8	177.0(2)
N6	Co3	N7	92.5(2)	N6	Co3	N8	94.6(2)
N7	Co3	N8	88.2(2)	O5	Co4	O6	81.9(1)
O5	Co4	N9	88.7(2)	O5	Co4	N10	95.2(2)
O5	Co4	N11	174.4(2)	O5	Co4	N12	88.2(2)
O6	Co4	N9	90.6(2)	O6	Co4	N10	177.1(2)
O6	Co4	N11	92.7(2)	O6	Co4	N12	87.2(2)
N9	Co4	N10	89.3(2)	N9	Co4	N11	92.8(2)
N9	Co4	N12	176.4(2)	N10	Co4	N11	90.2(2)
N10	Co4	N12	92.7(2)	N11	Co4	N12	90.1(2)
Co1	O1	Co2	97.6(2)	Co1	O2	Co2	98.1(1)
Co1	O3	Co3	95.7(2)	Co1	O4	Co3	97.4(1)
Co1	O5	Co4	98.0(2)	Co1	O6	Co4	97.8(2)
Anions							
O7	N13	O8	119.3(5)	O7	N13	O9	118.8(5)
O8	N13	O9	121.9(5)	O10	N14	O11	115.0(7)
O10	N14	O12	126.3(8)	O11	N14	O12	118.7(8)
O13	N15	O14	120.0(6)	O13	N15	O15	120.9(6)
O14	N15	O15	119.0(6)	O16	N16	O18	122.7(5)
O17	N16	O18	114.2(6)	O19	N17	O20	119.8(6)
O19	N17	O21	122.7(6)	O20	N17	O21	117.4(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Brief Historical Perspective of the Stereochemical Insight Displayed by Werner

There is little doubt that Werner became acquainted with the cobalt compounds Jørgensen was actively reporting on since 1878 [4] as a result of

TABLE VI Bond lengths, bond angles and hydrogen bonds for II

*Atom*1	*Atom*2	*Distance*	*Atom*1	*Atom*2	*Distance*
(A) Bond distances in angstroms					
Cation					
Co1	O1	1.903(1)	Co1	O2	1.911(1)
Co1	O3	1.911(1)	Co1	O4	1.918(1)
Co1	O5	1.908(1)	Co1	O6	1.909(1)
Co2	O1	1.912(1)	Co2	O2	1.920(1)
Co2	N1	1.964(2)	Co2	N2	1.949(2)
Co2	N3	1.958(2)	Co2	N4	1.963(2)
Co3	O3	1.926(1)	Co3	O4	1.938(1)
Co3	N5	1.941(2)	Co3	N6	1.947(2)
Co3	N7	1.940(2)	Co3	N8	1.958(2)
Co4	O5	1.929(1)	Co4	O6	1.921(1)
Co4	N9	1.950(2)	Co4	N10	1.939(2)
Co4	N11	1.953(2)	Co4	N12	1.963(2)
Anions					
N13	O7	1.222(2)	N13	O8	1.211(3)
N13	O9	1.240(2)	N14	O10	1.243(2)
N14	O11	1.235(2)	N14	O12	1.241(2)
N15	O13	1.231(2)	N15	O14	1.246(2)
N15	O15	1.251(2)	N16	O16	1.252(3)
N16	O17	1.248(3)	N16	O18	1.224(2)
N17	O19	1.212(3)	N17	O20	1.166(3)
N17	O21	1.208(4)	N18	O22	1.243(2)
N18	O23	1.248(3)	N18	O24	1.245(3)

*Atom*1	*Atom*2	*Atom*3	*Angle*	*Atom*1	*Atom*2	*Atom*3	*Angle*
(B) Bond angles in degrees							
Cation							
O1	Co1	O2	81.75(6)	O1	Co1	O3	93.60(6)
O1	Co1	O4	89.24(6)	O1	Co1	O5	95.90(6)
O1	Co1	O6	174.97(6)	O2	Co1	O3	175.07(6)
O2	Co1	O4	95.13(6)	O2	Co1	O5	89.65(6)
O2	Co1	O6	93.41(6)	O3	Co1	O4	83.12(6)
O3	Co1	O5	92.48(6)	O3	Co1	O6	91.27(6)
O4	Co1	O5	173.45(6)	O4	Co1	O6	92.57(6)
O5	Co1	O6	82.64(6)	O1	Co2	O2	81.27(6)
O1	Co2	N1	87.57(6)	O1	Co2	N2	94.65(7)
O1	Co2	N3	175.64(7)	O1	Co2	N4	89.60(6)
O2	Co2	N1	91.00(7)	O2	Co2	N2	175.86(6)
O2	Co2	N3	94.39(7)	O2	Co2	N4	87.89(7)
N1	Co2	N2	89.52(7)	N1	Co2	N3	92.08(7)
N1	Co2	N4	177.08(7)	N2	Co2	N3	89.69(8)
N2	Co2	N4	91.39(7)	N3	Co2	N4	90.69(7)
O3	Co3	O4	82.21(5)	O3	Co3	N5	91.85(7)
O3	Co3	N6	175.29(7)	O3	Co3	N7	92.26(7)
O3	Co3	N8	87.17(7)	O4	Co3	N5	86.55(6)
O4	Co3	N6	93.85(7)	O4	Co3	N7	173.67(7)
O4	Co3	N8	92.26(7)	N5	Co3	N6	90.49(8)
N5	Co3	N7	90.59(8)	N5	Co3	N8	178.55(8)
N6	Co3	N7	91.81(8)	N6	Co3	N8	90.42(8)

TABLE VI (Continued)

*Atom*1	*Atom*2	*Atom*3	*Angle*	*Atom*1	*Atom*2	*Atom*3	*Angle*
N7	Co3	N8	90.51(8)	O5	Co4	O6	81.76(6)
O5	Co4	N9	85.41(7)	O5	Co4	N10	93.34(7)
O5	Co4	N11	173.56(6)	O5	Co4	N12	93.69(7)
O6	Co4	N9	93.42(6)	O6	Co4	N10	173.96(7)
O6	Co4	N11	93.78(7)	O6	Co4	N12	85.83(6)
N9	Co4	N10	89.70(7)	N9	Co4	N11	90.24(8)
N9	Co4	N12	178.90(7)	N10	Co4	N11	91.38(8)
N10	Co4	N12	90.98(7)	N11	Co4	N12	90.61(8)
Co1	O1	Co2	98.74(6)	Co1	O2	Co2	98.22(6)
Co1	O3	Co3	97.65(6)	Co1	O4	Co3	96.99(6)
Co1	O5	Co4	97.67(6)	Co1	O6	Co4	97.92(6)
Anions							
O7	N13	O8	122.0(2)	O7	N13	O9	117.7(2)
O8	N13	O9	120.3(3)	O10	N14	O11	119.3(2)
O10	N14	O12	120.2(2)	O11	N14	O12	120.4(2)
O13	N15	O14	122.3(2)	O13	N15	O15	119.0(2)
O14	N15	O15	118.7(2)	O16	N16	O17	118.6(2)
O16	N16	O18	121.1(2)	O17	N16	O18	120.3(3)
O19	N17	O20	125.8(3)	O19	N17	O21	120.0(3)
O20	N17	O21	114.2(3)	O22	N18	O23	120.8(2)
O22	N18	O24	119.8(2)	O23	N18	O24	119.3(2)

A—H Distance		*A—H....O Angle*		*Symmetry position if not x, y, z*
(C) Hydrogen bonds(distances in Å, angles in °)				
Intraionic Contacts				
O1—H20	1.966(1)	N5—H20...O1	153.8(1)	
O3—H40	2.060(1)	N12—H40...O3	154.7(1)	
O4—H7	2.050(1)	N1—H7...O4	152.5(1)	
O5—H16	2.133(1)	N4—H16...O5	152.0(1)	
Interionic Contacts				
O7—H8	2.268(2)	N1—H8...O7	161.0(1)	07 at 1 − *x*, −*y*, −*z*
O7—H14	2.275(2)	N3—H14...O7	144.9(1)	07 at 1 − *x*, −*y*, −*z*
O7—H33	2.239(2)	N9—H33...O7	170.2(1)	
O9—H12	2.257(2)	N2—H12...O9	169.2(1)	09 at *x* − 1, *y*, *z*
O9—H38	2.270(2)	N11—H38...O9	169.0(1)	
O10—H9	2.238(2)	N1—H9...O10	160.5(1)	010 at −*x*, 1 − *y*, 1 − *z*
O10—H35	2.169(2)	N10—H35...O10	148.2(1)	010 at 1 − *x*, 1 − *y*, 1 − *z*
O11—H10	2.237(2)	N2—H10...O11	155.2(1)	011 at −*x*, 1 − *y*, 1 − *z*
O11—H19	2.083(2)	N5—H19...O11	173.2(1)	
O12—H42	2.125(2)	N12—H42...O12	157.6(1)	012 at 1 − *x*, 1 − *y*, 1 − *z*
O13—H18	2.155(2)	N4—H18...O13	150.1(1)	013 at 1 − *x*, −*y*, −*z*
O14—H2	1.819(2)	O2—H2...O14	167.4(1)	
O15—H6	1.909(2)	O6—H6...O15	165.8(1)	
O15—H15	2.129(2)	N3—H15...O15	157.4(1)	015 at 1 − *x*, −*y*, −*z*
O16—H4	2.287(2)	O4—H4...O16	142.0(1)	016 at −*x*, 1 − *y*, −*z*
O16—H24	2.034(2)	N6—H24...O16	170.4(1)	
O17—Hw1	1.735*	Ow1—Hw1...O17	143.5(2)	017 at 1 + *x*, *y*, *z*
O17—H30	2.197(2)	N8—H30...O17	140.3(1)	017 at −*x*, 1 − *y*, −*z*
O17—H37	2.130(2)	N11—H37...O17	150.9(1)	017 at 1 + *x*, *y*, *z*

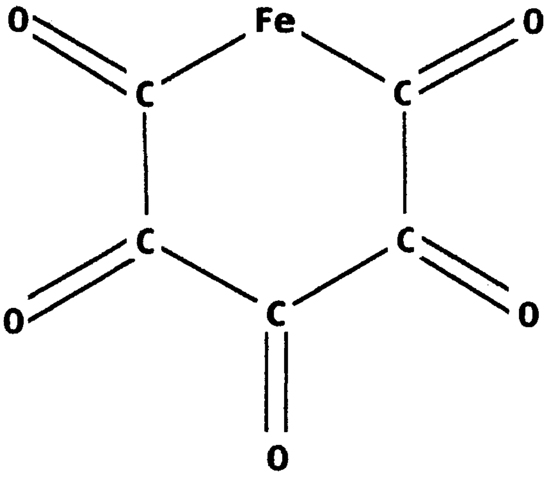
TABLE VI (Continued)

A—H Distance		*A—H....O Angle*		*Symmetry position if not x, y, z*
O18—H21	2.136(2)	N5—H21...O18	160.3(1)	
O23—H36	2.225(2)	N10—H36...O23	135.5(1)	023 at $1+x$, $1-y$, z
O24—H25	2.038(2)	N7—H25...O24	168.7(1)	
O24—Hw4	1.819*	Ow2—Hw4...O24	157.5(2)	024 at $-x$, $1-y$, $1-z$
Ow2—H1	1.725*	O1—H1...Ow2	159.5(1)	

Number in parentheses are estimated standard deviations in the least significant digits.

* These distances may vary from the reported values due to difficulty in positioning the water hydrogens.

his interest in the bonding of nitrogen and, more specifically, in the structure of the ammonium cations [16]. The scientific offspring of his new chemical studies was the proposal of one of the milestones of chemistry, a description of which is best left to his distinguished biographer [1], who declared that "occasionally, one man may play such a central role in a particular field of science that his name becomes synonymous with that field. Alfred Werner, the undisputed founder and systematizer of coordination chemistry, is just such a man. Even today, more than a half-century after his death, coordination compounds, particularly metal-ammines, are still known as Werner complexes, and coordination theory is colloquially called Werner's theory". ...." and it is no exaggeration to declare that his coordination theory exerted an effect on inorganic chemistry comparable to that exerted on organic chemistry by the structural ideas of Kekule, Couper, Le Bel and van't Hoff".



SCHEME 1

Prior to Werner's theory of the nature and structure of coordination compounds, these substances were largely formulated using the bonding ideas of Blomstrand and his followers [17]. Such descriptions were heavily influenced by the concepts of organic chemists of the day; and, as late as 1910, Erdmann's book [18] describes $Fe(CO)_5$ as having the structure shown below – a formulation which was, no doubt, influenced by that of quinones.

It was against such a background that Werner re-formulated the inorganic compounds we now name after him, and the enormity of this intellectual synthesis, when placed within the scientific beliefs surrounding him is still a source of wonderment.

The Hexol Clusters

In 1888, Jørgensen had reported the syntheses of compounds containing cations which he described as being di-nuclear [19a]. In 1907, Werner reformulated them as tetra-nuclear [19b] and assigned to them the modern composition all of us are now familiar with: $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$. In our view, it is remarkable that this impressive feat of chemical insight and structural imagination was accomplished in the face of the then accepted bonding theories mentioned above and in the absence of any of the stereochemical aid tools we now take for granted.

Although, he saw his monumental work honored with the Nobel Prize of 1913, certain aspects of his theory were not fully documented at the time of his early death (15th November, 1919). Thus, we wish to commemorate the 109th year of the completion of his doctoral studies with an investigation of ours touching on one of the more crucial aspects of his opus: the recognition of the nature of the tetra-nuclear cations of composition $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ and the chirality implications such stereochemical formulation had, if correct. In those days, both topics were rather controversial, to put it mildly [16].

Amazingly, with a single masterful stroke, Werner realized [19] that such cations should be optically active, while containing no carbon atoms – the Achilles heel of the polarimetric measurements of his recently resolved $[Co(en)_2(NH_3)Cl]X$ compounds [20] was that they contained organo-carbon ligands, assumed by his scientific adversaries to be the origin of the optical rotations recorded by him and King [20]. It was a full confirmation of this latter aspect of his monumental scientific achievements which he was not fortunate enough to see finished, for the structure of one of these species, alone, provides unquestionable confirmation of both, his theory of the stereochemistry of nitrogen (the theme of his dissertation); and, more importantly, of the stereochemistry and origin of the optical activity of Co(III) complexes – a purely intellectual conception with which Werner made a giant stride at establishing the universality of stereochemical principles.

DISCUSSION

Physical Properties of the Clusters

Cyclic voltametry of these cations show irreversible, severely distorted oxidation and reduction waves indicative of chemical processes following the electrode processes. Thus, one would not expect mixed valence state species to be sufficiently long lived to become incorporated into crystals which take many hours or days to be deposited in the crystallization dishes.

^{1}H-nmr measurements of solutions in DMSO show very sharp lines with very modest shifts, results which could not be expected from a paramagnetic Co cluster that would be expected to produce broad NMR lines and/or very large, paramagnetically induced, chemical shifts.

The magnetic susceptibility of (I) shows a small, positive X'_m indicating probable admixture of a relatively low-lying, excited spin multiplet. However, given the remarks in the preceding paragraphs it seems unlikely that the observed value of the susceptibility is due to Co(II) or Co(IV) impurities.

The combined results of the magnetic susceptibility and of the ^{1}H-nmr of compound (I) indicate the cations have a ground state spin singlet, as expected for octahedral compounds of Co(III) similar in nature to the diamagnetic $[Co(NH_3)_4X_2]^{n+}$ cations; thus, the intensely brown–black color of solutions of these compounds is not the result of mixed [Co(II)–Co(III)] or of [Co(III)–Co(IV)] valence states in these substances, rather it is probably due to charge transfer processes.

Stereochemical Properties of the Compounds

The Chiral Properties of the Cations

Although both compounds crystallize in centrosymmetric space groups, and both enantiomers are present in each lattice, the correct chirality description of the central Co1 in Figure 1, is Λ; however, nothing further can be said about the remaining chiral centers (OH, see below) of that cation. In the case of (**II**), if proper account is taken of the non-bonded pair at each of the six bridging OH ligands, one notes that they are also chiral centers, each of them being (S) for the species shown in Figures 3–5. Therefore, since the central Co1 atom is Λ, the complete chiral descriptor symbol for this cation is $\Lambda[S^6\text{-(hexa-}\mu\text{-OH)}]$. That is, this cation has six more chiral centers than was suspected by Werner, who had no reason to understand the stereochemical role of non-bonded pairs located at the oxygens of the OH bridges – a concept not then understood.

Ion Pairing Effects in the Lattice

The nature of the cation present in the asymmetric unit of (**I**) is depicted in Figure 1, which shows the central Co(III) cation surrounded by three bidentate $[Co(NH_3)_4(OH)_2]^+$ cations, exactly as visualized by Werner. The heavy atom skeleton depicted in Figure 1 clearly shows the chiral nature of Co1, which in this case is Λ. However, little else can be said about this cation since its hydrogen atoms were not found at reasonable places. This is lamentable but has been corrected by the more accurate and precise results obtained with compound (**II**), see below. Nonetheless, we feel that presentation of the results obtained with (**I**) are worth publishing since, if nothing else, the synthesis of the cluster *via* a thermally-induced, hydrolytic cleavage of the mononuclear cation $[Co(NH_3)_4(NO_2)_2]^+$ has never been described before. The preparation of the hexol cluster in (**II**), starting with the carbonato cation $[Co(NH_3)_4(CO_3)]^+$ is equally novel.

The cations in (**II**) are depicted in Figures 2 and 3; the former figure is intended to show the detailed stereochemistry of the cation and the numbering system used in the crystallographic analysis. The latter figure shows the cation and the surrounding anions with enough labels to identify the hydrogen bonds linking cations, anions and waters. The structural study of (**I**) did not yield hydrogens at reasonable positions; thus, they were left out of the analysis. Such was not the case with (**II**) in which all hydrogens, with the exception of one water hydrogen, were found experimentally at very reasonable positions. Most importantly, the hydrogens of the μ-hydroxo bridges appeared in early difference maps at excellent positions, as judged by the O—H distances (the ave. O—H distance is 0.987 Å and the range is from 0.947 Å to 1.061 Å). As in the case of (**I**) and as was predicted by Werner, there is a central Co(III) cation bearing three bi-dentate ligands of composition $[Co(NH_3)_4(OH)_2]^+$ which complete the octahedron around the central cation.

Comparison of the Stereochemistry of the Cations in (I) and (II)

Let us make a brief comparison of the heavy atom skeletons in (**I**) and (**II**) to document their near identity, and then, proceed to discuss the stereochemical details of these clusters from the viewpoint of the data obtained with the latter compound.

The Co1—O distances in (**I**) range from 1.895(3) to 1.920(3) Å, with an average value of 1.907(3) Å while in (**II**) these bonds range from 1.903(1) to 1.918(1) Å and average to 1.910(1) Å. Given the uncertainties involved in the measurements, these averages are essentially the same. The Co1—N distances in (**I**) range from 1.951(5) to 1.987(4) Å and average 1.953(4) Å, while those in (**II**) range from 1.939(2) to 1.964(2) Å, which average to 1.945(2) Å; again, the difference between averages is small, if any. The Co1—Co distances for (**I**) are 2.896, 2.888 and 2.889 Å, and their average is 2.891 Å. In (**II**), they are 2.881, 2.876 and 2.874 Å, while their average is 2.877 Å. Finally, the angles Co—O—Co of (**I**) range from 95.7(2)° to 98.1(1)° and average 97.4(2)°; the relevant values for (**II**) are: range = 96.99(6)° to 98.74(6)° and average = 97.87(6)°. Thus, the results obtained for (**I**), while of somewhat lower precision than those encountered in (**II**) are, more or less, equally accurate. With that comment, we proceed to discuss the meaning of the more accurate and precise stereochemical parameters of the hexol cation obtained for (**II**).

The Co—N distances of the two — NH_3 ligands, *trans* to one another, are 1.964(1), 1.963(2), 1.941(2), 1.958(2), 1.950(2) and 1.963(2) Å, which average to 1.957(2)Å. The relevant values for the Co—N bonds *trans* to the OH bridges are 1.949(2), 1.958(2), 1.947(2), 1.940(2), 1.939(2) and 1.953(2) Å, averaging 1.948(2) Å. Thus, we see the expected difference due to the lower *trans* influence of the OH ligands as compared with that of — NH_3 ligands.

Among the structural studies of Co—NH_3 bearing species, that of $[Co(NH_3)_6][Co(CN)_6]$, studied by Iwata, Saito *et al.* [21] produced a value of the Co—N distances of 1.968(1) Å. Other accurate determinations of the Co—$N(NH_3)$ distances give: 1.960(6) Å [22] and 1.968(2) Å (neutron diffraction of $[Co(NH_3)_6][CuCl_5]$) [23]. In both cases, our values, above, are in satisfactory agreement with these.

The Stereochemistry of the Anions

The N—O distances of the NO_3- anions range from 1.211(3) to 1.248(3) Å and the average is 1.237(3) Å – values which are in good agreement with those for NH_4NO_3 (Phase III; neutron diffraction) [24] in which the relevant values were 1.237(3) and 1.240(2) Å.

The above analysis establishes the descriptive quality of the heavy atom framework in the structural determination of the fragments present in (**II**).

Inter and Intramolecular Hydrogen Bonding Effects

It is clear from our previous comments on the mass spectrometry that the cations and anions are strongly associated as ion pairs even in the chamber of a mass spectrometer. This result is substantiated by the hydrogen bonded scheme shown in Figure 3 and the numerical data on Table VI(c). The shortest intermolecular contacts for the H's on the bridging OH ligands are O14—H2 = 1.819 Å, with O2—H2....O14 = 167.4° and O15—H6 = 1.909, with O6—H6....O15 = 165.8°. The inter-ionic hydrogen bonds between the nitrate anions and the NH_3 hydrogens range from 2.125 to 2.287 Å and have reasonably good NH....O angles. What is more remarkable is the shortness of some of the intramolecular hydrogen bonds. For example, O1—H2O is 1.966 Å and the N—H....O angle is 153.8°.

CONCLUSION

The structures of two species bearing Werner's hexol cation were established by X-ray diffraction methods. One was of excellent quality and allowed the location of the hydrogen atoms present in the entire cation. Thus, it was possible to establish the absolute configuration of the OH bridges, relative to the configurational symbol for the central Co(III) cation – namely, for a central Co to be Λ, all six of the OH bridges are S.

Upon succeeding in separating the antipodes of the hexol cations, Werner stated (see Ref. [1]) that "carbon-free inorganic compounds can also exist as mirror-image isomers" and therefore "the difference still existing between carbon compounds and purely inorganic compounds disappears".

We feel Werner would have been pleased upon being informed of these results, which we report in honor of his extraordinary gifts as an inorganic chemist and as a stereochemical pioneer.

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Supplementary Material

A table listing the coordinates and thermal parameters of all atoms present in (II), including the hydrogen atoms of all species therein, except for one missing hydrogen of a water of crystallization are available from IB.

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