American Chemical Society, for partial support of this research.

Registry No. [Cu(terpy)CN](NO_3)·H_2O, 58846-95-0.

Supplementary Material Available: Table VI, a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Colorado State University. (b) Western Washington State College.
(2) O. P. Anderson, *Inorg. Chem.*, **14**, 730 (1975).
(3) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Wiley, New York, N.Y., 1972, p 907.
(4) Y. M. Curtis and N. F. Curtis, *Aust. J. Chem.*, **19**, 609 (1966).
(5) M. Wicholas and T. Wolford, *Inorg. Chem.*, **13**, 316 (1974).
(6) R. Jungst and G. Stucky, *Inorg. Chem.*, **13**, 2404 (1974).
(7) D. F. Shriver, *Struct. Bonding (Berlin)*, **1**, 39 (1966); A. Ludi and H. U. Güdel, *ibid.*, **14**, 1 (1973).
(8) D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **96**, 3443 (1974).
(9) B. J. Hathaway, *Struct. Bonding (Berlin)*, **14**, 49 (1973).
(10) T. J. Kistenmacher and D. J. Szalda, *Acta Crystallogr., Sect. B*, **31**, 1659 (1975).
(11) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969.
(12) Using the automated routines incorporated in the Enraf-Nonius diffractometer package.
(13) The following programs were used in this structure determination: Zalkin's FORDAP Fourier program; AGNOST, an absorption correction program; Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; Ibers' CELREF for least-squares refinement of cell parameters; ORFFE, Busing and Levy's function and error program; ORTEP, Johnson's thermal ellipsoid plot program. The program for data reduction and *Lp* correction was locally written for the CDC 6400 computer.
(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(15) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(16) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(17) E. N. Maslen, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1803 (1974).
(18) D. V. Naik and W. R. Scheidt, *Inorg. Chem.*, **12**, 272 (1973).
(19) O. P. Anderson, *J. Chem. Soc., Dalton Trans.*, 2597 (1972).
(20) O. P. Anderson, *J. Chem. Soc., Dalton Trans.*, 1237 (1973).
(21) S. C. Yang and P. W. R. Corfield, Abstracts, American Crystallographic Association Meeting, University of Connecticut, Storrs, Conn., 1973, No. M8.
(22) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 158 (1970).
(23) T. J. Kistenmacher, T. Sorrell, and L. G. Marzilli, *Inorg. Chem.*, **14**, 2479 (1975).
(24) F. S. Stephens, *J. Chem. Soc.*, 2493 (1969).
(25) G. Davey and F. S. Stephens, *J. Chem. Soc.*, 103 (1971).
(26) R. J. Williams, D. T. Cromer, and A. C. Larson, *Acta Crystallogr., Sect. B*, **27**, 1701 (1971).
(27) R. J. Williams, D. T. Cromer, and A. C. Larson, *Acta Crystallogr., Sect. B*, **28**, 858 (1972).
(28) B. C. Wang, W. P. Schaefer, and R. W. Marsh, *Inorg. Chem.*, **10**, 1492 (1971).
(29) F. R. Fronczek and W. P. Schaefer, *Inorg. Chem.*, **13**, 727 (1974).
(30) *Chem. Soc., Spec. Publ.*, **No. 11**, M141 (1958).
(31) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(32) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif., 1960; W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968.
(33) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Synthesis and Characterization of Cobalt(III) Complexes Containing a Coordinated Selenol. A Structural Trans Effect in (2-Selenolatoethylamine-*N*,*Se*)bis(ethylenediamine)cobalt(III) Nitrate

CY A. STEIN, PAUL E. ELLIS, Jr., R. C. ELDER,* and EDWARD DEUTSCH

Received December 23, 1975 AIC509169

The synthesis and characterization of (2-selenolatoethylamine-*N,Se*)bis(ethylenediamine)cobalt(III) and (2-selenolacetato-*O,Se*)bis(ethylenediamine)cobalt(III) salts are described. These complexes are the first well-defined examples of selenol coordination to cobalt(III). Coordinated selenols and thiols give rise to intense chalcogen-to-metal charge-transfer bands in the uv absorption spectra; the positions of these bands show that coordinated selenols are better reductants than the analogous coordinated thiols. A single-crystal x-ray structure analysis of the title compound shows that the average Co–N distance for those nitrogen atoms bonded cis to selenium is 1.971 (9) Å, whereas the trans Co–N length is 2.034 (2) Å. This corresponds to a ground-state trans effect, induced by the coordinated selenol, of 0.063 (9) Å which is larger than the 0.041 (10) Å effect of coordinated thiol in the analogous (2-thiolatoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) ion. The influence of hydrogen bonding on the bond lengths and the conformation of the complex is discussed.

Introduction

Recent studies on the biochemical roles of selenium have indicated that this element is often associated with transition metals and electron-transfer processes.[1,2] The interactions between selenium (particularly as selenol) and transition metals are also of interest to us because of the periodic relationship between selenium and sulfur vis-à-vis recent reports on the remarkable properties of robust cobalt(III) and chromium(III) complexes containing coordinated thiols.[3] One particular property, the induction of a significant structural trans effect by thiolato sulfur in cobalt(III) complexes,[3d] may underlie several of the observed chemical and kinetic effects induced by coordinated sulfur.[3f–5] We therefore thought it worthwhile to probe the extent of the ground-state trans effect phenomenon in octahedral complexes by investigating selenol analogues to the thiol complexes which exhibit both trans effects and unusual chemical properties. This paper describes the syntheses of two such complexes and the results of a single-crystal x-ray structure analysis of one of these compounds. To our knowledge these are the first well-defined selenolatocobalt(III) complexes to be reported.[6] Since these particular species are also robust and contain only "soft" Se and "hard" N and O as ligating atoms, they not only significantly extend the known types of selenol–metal complexes[7] but also provide useful models with which to probe biologically important selenium–metal interactions.

Experimental Section

General Data. Common laboratory chemicals were of reagent grade. Visible–uv spectra were recorded on a Cary 14 spectrophotometer at ambient temperature. Melting points (Thomas-Hoover apparatus) were obtained in open capillaries and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Bis(2-ammonioethyl) Diselenide Sulfate, $(H_3NCH_2CH_2Se-)_2[SO_4]$. This compound was prepared by the method of Klayman[8] and then recrystallized two times from water–ethanol; mp 279–281 °C (lit. mp 277–279 °C). Anal. Calcd for $C_4H_{14}N_2O_4SSe_2$: C, 13.96; H, 4.10; N, 8.14; Se, 45.88. Found: C, 14.17; H, 4.04; N, 8.23; Se, 45.94. Preparation of this compound by the method of Gunther[9] was completely unsuccessful in our hands.

Diselenodiacetic Acid, $(HOOCCH_2Se-)_2$. Disodium diselenide prepared by the method of Klayman and Griffin[10] was added to potassium chloroacetate according to the procedure of Backer and Van Dam.[11] Acidification and purification of this product mixture (several crystallizations from acetone–benzene and acetone–xylene) yielded crude diseleniumdiacetic acid that was contaminated with chloroacetic acid. This material could not be readily purified further but was found to be satisfactory for use in subsequent reactions.

(2-Selenolatoethylamine-*N*,*Se*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(SeCH_2CH_2NH_2)](ClO_4)_2$. In a typical preparation, 0.029 mol of cobaltous perchlorate was dissolved in 30 ml of water and the solution deaerated with a stream of nitrogen. To this solution were successively added 70 ml of deaerated 10% (v/v) ethylenediamine (0.10 mol) and then a deaerated solution of 0.0145 mol of bis(2-ammonioethyl) diselenide sulfate in 25 ml of water, the reaction mixture being continuously stirred and deaerated. After 30 min the reaction mixture was opened to the atmosphere, filtered, combined with an equal volume of saturated sodium perchlorate solution, and refrigerated (4 °C) overnight. The resulting brown needles were recrystallized from 75 ml of warm 2 *F* sodium perchlorate, the final product yield being 53%. Anal. Calcd for $C_6H_{22}N_5SeCo(ClO_4)_2$: C, 14.38; H, 4.43; N, 13.98; Se, 15.76; Co, 11.76; Cl, 14.15. Found: C, 14.43; H, 4.31; N, 13.99; Se, 15.60; Co, 11.59; Cl, 13.97. The perchlorate salt can be converted into the thiosulfate salt by simple metathesis with sodium thiosulfate. Anal. Calcd for $C_6H_{22}N_5SeCo(S_2O_3)$: C, 17.39; H, 5.35; N, 16.91; Se, 19.06; Co, 14.22; S, 15.48. Found: C, 17.32; H, 5.18; N, 17.01; Se, 19.42; Co, 14.36; S, 15.60.

(2-Selenolatoethylamine-*N*,*Se*)bis(ethylenediamine)cobalt(III) Nitrate, $[(en)_2Co(SeCH_2CH_2NH_2)](NO_3)_2$. This salt may be made directly from the above perchlorate salt by simple metathesis with sodium nitrate, or the above procedure may be followed using cobaltous nitrate and sodium nitrate in place of the respective perchlorate salts. In the latter case, the total yield of recrystallized material is 60%. Crystals suitable for x-ray structural analysis were grown by slow cooling (ca. 12 h) of a saturated aqueous solution of the nitrate salt from 50 to 4 °C. Anal. Calcd for $C_6H_{22}N_5SeCo(NO_3)_2$: C, 16.91; H, 5.20; N, 23.00; Se, 18.53; Co, 13.83. Found: C, 16.75; H, 5.20; N, 22.78; Se, 18.57; Co, 13.83.

(2-Selenolatoacetato-*O*,*Se*)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(SeCH_2COO)](ClO_4)$. The above procedure for the synthesis of $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ was followed as closely as possible, allowing for the fact that our sample of diselenodiacetic acid was impure (vide supra) and thus an exact cobalt:diselenide ratio of 2.0 could not be ensured. The initial yield of red crystalline product was recrystallized from a saturated (room temperature) solution by addition of a half-volume of a saturated solution of sodium perchlorate (final yield 25% based on cobalt). Anal. Calcd for $C_6H_{18}N_4O_2SeCo(ClO_4)$: C, 17.34; H, 4.37; N, 13.48; Se, 19.00; Co, 14.18. Found: C, 17.26; H, 4.32; N, 13.61; Se, 18.70; Co, 13.89.

X-Ray Characterization. Precession photographs taken of crystals of the formula $[(en)_2Co(SeCH_2CH_2NH_2)](NO_3)_2$ revealed monoclinic symmetry. The systematic absences apparent on photographs of the *hk*0, *hk*1, *h*0*l*, and *h*1*l* layers were for *h*0*l*, *h* + *l* odd, and for 0*k*0, *k* odd, indicating space group $P2_1/n$.[12] These observations were confirmed in the intensity data collection and the choice of space group was substantiated by the subsequent successful refinement.

Table I. Absorption Spectra of Analogous Thiolato and Selenolato Cobalt(III) Complexes[a]

$[(en)_2Co(XCH_2CH_2NH_2)]^{2+}$		$[(en)_2Co(XCH_2COO)]^{+}$	
X = S	X = Se	X = S	X = Se
482 (140)	490 (170)	516 (180)	520 (150)
282 (14 000)	297 (18 500)	282 (12 000)	295 (17 000)

[a] In aqueous perchloric acid media at 25 °C. Entries are peak positions in nm; values inside parentheses are molar extinction coefficients in M^{-1} cm^{-1}.

A triangular prism of the material approximately 0.4 mm long and 0.25 mm along the edge of a triangular face was mounted with its long dimension coincident with a glass fiber axis. This crystal was placed on a Syntex $P\bar{1}$ diffractometer equipped with graphite monochromator and molybdenum target tube (Mo Kα, λ 0.710 69 Å). Fifteen reflections were precisely centered and cell constants determined by least-squares analysis of the measured 2θ values are $a = 9.488$ (2) Å, $b = 12.923$ (3) Å, $c = 12.725$ (4) Å, $\beta = 98.44$ (1)°. All measurements were made at 21 + 3 °C. Density measurements made by neutral buoyancy techniques in $CHCl_3-CHBr_3$ (d_{measd} = 1.83 (3) g cm^{-3}, d_{calcd} = 1.81 g cm^{-3}) indicated $Z = 4$ and thus there is no necessary crystallographic symmetry in either the cation or the anions. Crystal quality and the correctness of indexing were checked by taking oscillation photographs (±14°) about each of the crystal axes.

Intensity measurements for 2725 reflections in the sphere $2\theta < 46°$ were made as previously described.[3d] The asymmetric $\theta-2\theta$ scan was from 0.7° below to 0.8° above the reflection in 2θ. Scan rates varied from 1.0 to 8.0°/min depending on the intensity of the reflection. Four standard reflections were used to check stability and to account for long-term drift. The drift correction varied from 1.010 to 0.993. Absorption corrections were applied[13] since μ, the linear absorption coefficient, was 37.5 cm^{-1}. The transmission factors ranged from 0.61 to 0.52. The proper application of these corrections was checked by measuring the standard reflections at every 5° in rotation about the diffraction vector and comparing the observed intensity with the calculated transmission coefficient.[14] A set of 2169 unique normalized structure factors was obtained by averaging equivalent reflections. Of these, 1951 were considered observed ($I > 2\sigma(I)$), where a value of 0.02 was used for *p*, the Ibers ignorance factor.[15] All reflections were used in subsequent refinement.

Solution and Refinement of Structure. A Patterson map[16] was computed and the positions of the selenium and cobalt atoms were determined. An electron density map computed using signs based on these two atom positions revealed the positions of the 19 remaining nonhydrogen atoms. Five cycles of least-squares refinement of scale factor, atom positions, and isotropic thermal parameters gave R_1 = 0.12.[17] Two additional cycles of refinement with anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.046$ and R_2 = 0.064. A difference Fourier map indicated positions of 21 of the hydrogen atoms. Fixed hydrogen atoms were included at their calculated positions (C–H = 1.00 and N–H = 0.90 Å). Convergence of the model with fixed hydrogen atoms was reached at $R_1 = 0.027$, $R_2 = 0.033$. Continued refinement using a blocked-diagonal technique and refining hydrogen atom positional and isotropic thermal parameters as well as positional and anisotropic thermal parameters for all other atoms converged to $R_1 = 0.023$, $R_2 = 0.024$, and $R_3 = 0.076$, using 2169 intensities to refine 278 variables (88 hydrogen atom variables). In the last cycle of refinement the maximum shift per error was 0.8 and the average shift per error was 0.1. A final difference map was essentially featureless; the largest peak was less than 0.03 the height of a carbon atom peak on the same scale. The final error of an observation of unit weight was 1.52. Examination of groups of reflections ordered on $|F_o|$ indicated that the most intense reflections were probably overweighted and that a larger value of *p* (vide supra) would have been preferable. The scattering curves used were those for Se, Co, O, N, C,[18] and H.[19] Corrections for anomalous dispersion[20] were made using $\Delta f' = -0.1$ and $\Delta f'' = 2.4$ for selenium and $\Delta f'$ = 0.4 and $\Delta f'' = 1.1$ for cobalt. The values of $|F_o|$ and F_c are listed in Table A.[21]

Results

Characterization of Complexes. The $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SeCH_2COO)]^{+}$ ions are characterized by (1) elemental analyses of the isolated salts which give empirical compositions in agreement with those predicted from the proposed formulations (see Experimental Section), (2) cation-exchange elution characteristics which are consistent with the assigned formal charges, and (3) visible–uv absorption spectra which are analogous to the comparable thiolato complexes (see Table I). In this latter context, the intense absorption bands in the 280–300-nm region should be especially noted; for the thiolato complexes these bands have

Table II. Fractional Atomic Positional Parameters[a,b]

Atom	*x*	*y*	*z*
Co	0.179 40 (3)	0.231 65 (2)	0.521 61 (2)
Se	0.066 87 (3)	0.139 35 (2)	0.370 56 (2)
C(1)	0.249 5 (3)	0.091 3 (3)	0.335 5 (2)
C(2)	0.342 5 (3)	0.062 6 (2)	0.435 3 (2)
N(1)	0.353 8 (2)	0.149 6 (2)	0.513 0 (2)
N(2)	0.239 4 (3)	0.341 9 (2)	0.431 5 (2)
C(3)	0.296 0 (3)	0.431 8 (2)	0.497 4 (2)
C(4)	0.377 8 (3)	0.392 7 (2)	0.599 7 (2)
N(3)	0.286 3 (3)	0.315 3 (2)	0.643 4 (2)
N(4)	0.001 7 (2)	0.306 2 (2)	0.531 1 (2)
C(5)	−0.062 1 (2)	0.264 4 (2)	0.621 2 (2)
C(6)	−0.044 4 (3)	0.149 5 (2)	0.619 9 (3)
N(5)	0.109 1 (3)	0.130 5 (2)	0.618 0 (2)
N(6)	0.134 5 (3)	0.213 4 (2)	0.895 8 (2)
O(1)	0.018 4 (2)	0.177 6 (2)	0.860 4 (2)
O(2)	0.142 7 (3)	0.268 5 (2)	0.975 2 (2)
O(3)	0.240 0 (2)	0.196 0 (2)	0.852 4 (1)
N(7)	0.443 6 (2)	0.030 6 (2)	0.773 2 (2)
O(4)	0.485 9 (2)	0.009 8 (1)	0.868 4 (1)
O(5)	0.496 2 (2)	0.106 3 (1)	0.733 3 (1)
O(6)	0.350 1 (2)	−0.022 4 (1)	0.720 5 (1)

[a] The estimated errors in the last digit are given in parentheses. This form is used throughout. [b] The numbering scheme is shown in the figures.

Table III. Rms Displacements (Å)

Atom	Min	Mean	Max
Co	0.160	0.167	0.178
Se	0.179	0.193	0.221
C(1)	0.194	0.232	0.236
C(2)	0.201	0.223	0.238
N(1)	0.172	0.195	0.210
N(2)	0.175	0.186	0.192
C(3)	0.182	0.205	0.230
C(4)	0.176	0.218	0.232
N(3)	0.168	0.195	0.208
N(4)	0.158	0.186	0.217
C(5)	0.181	0.209	0.234
C(6)	0.191	0.219	0.234
N(5)	0.176	0.193	0.214
N(6)	0.187	0.211	0.286
O(1)	0.208	0.296	0.411
O(2)	0.260	0.290	0.440
O(3)	0.193	0.236	0.339
N(7)	0.179	0.197	0.225
O(4)	0.185	0.217	0.296
O(5)	0.208	0.230	0.273
O(6)	0.207	0.250	0.286

Table IV. Bond Lengths (Å)

Co–Se	2.378 (1)	Co–N(3)	2.034 (2)
Co–N(1)	1.982 (2)	Co–N(4)	1.961 (2)
Co–N(2)	1.965 (2)	Co–N(5)	1.975 (3)
Se–C(1)	1.952 (3)	N(1)–C(2)	1.491 (4)
C(1)–C(2)	1.483 (4)	N(2)–C(3)	1.486 (3)
C(3)–C(4)	1.501 (4)	N(3)–C(4)	1.485 (4)
C(5)–C(6)	1.494 (4)	N(4)–C(5)	1.476 (4)
C–C(av)	1.493 (9)	N(5)–C(6)	1.480 (4)
		N–C(av)	1.484 (6)
N(6)–O(1)	1.218 (3)	N(7)–O(4)	1.248 (3)
N(6)–O(2)	1.228 (4)	N(7)–O(5)	1.239 (3)
N(6)–O(3)	1.233 (3)	N(7)–O(6)	1.237 (3)
		N–O(av)	1.234 (10)

Table V. Bond Angles (deg)

	Metal Coordination Angles		
Se–Co–N(1)	88.07 (6)	Se–Co–N(3)	175.48 (18)
Se–Co–N(2)	91.52 (6)	Se–Co–N(4)	90.47 (6)
Se–Co–N(5)	90.99 (7)	N(1)–Co–N(3)	89.96 (9)
N(1)–Co–N(5)	92.38 (10)	N(2)–Co–N(4)	90.28 (10)
N(3)–Co–N(4)	91.68 (9)	N(4)–Co–N(5)	85.14 (10)
N(1)–Co–N(2)	92.26 (10)	N(1)–Co–N(4)	177.10 (13)
N(2)–Co–N(3)	84.49 (9)	N(2)–Co–N(5)	174.79 (11)
N(3)–Co–N(5)	93.15 (9)		
	Ligand Angles		
N(1)–C(2)–C(1)	110.8 (2)	C(1)–Se–Co	92.1 (1)
N(2)–C(3)–C(4)	108.9 (2)	C(2)–N(1)–Co	117.5 (2)
N(3)–C(4)–C(3)	107.2 (2)	C(3)–N(2)–Co	110.5 (2)
N(4)–C(5)–C(6)	107.2 (2)	C(4)–N(3)–Co	109.1 (2)
N(5)–C(6)–C(5)	106.1 (2)	C(5)–N(4)–Co	108.8 (2)
N–C–C(av)	108 (2)	C–N–Co(av)	111 (4)
	Nitrate Angles		
O(1)–N(6)–O(2)	117.9 (3)	O(4)–N(7)–O(5)	118.4 (2)
O(1)–N(6)–O(3)	121.0 (2)	O(4)–N(7)–O(6)	120.6 (2)
O(2)–N(6)–O(3)	121.1 (2)	O(5)–N(7)–O(6)	121.0 (2)

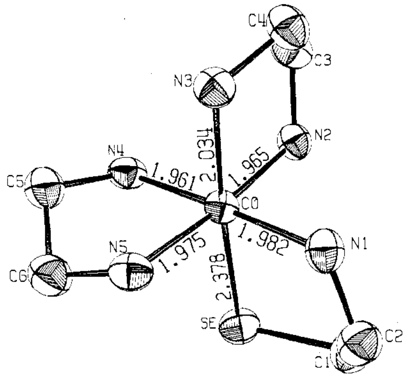

Figure 1. Structure of the complex cation of (2-selenolatoethylamine-*N*,*Se*)bis(ethylenediamine)cobalt(III), shown looking down the psuedo-threefold axis. The Δ(λ′λδ) enantiomer is shown where λ′ is the conformation of the selenol chelate. The crystal contains both the Δ and Λ partners of the enantiomeric pair. Hydrogen atoms have been omitted for clarity. The ellipsoids represent 50% probability and selected bond lengths are given in Å.

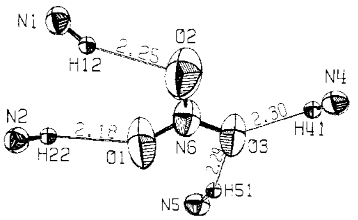

Figure 2. One of two nitrate ions and the associated hydrogen-bonded amine groups. The orientation is chosen to illustrate the relatively large thermal motion of the anion.

been assigned[22] to be ligand-to-metal charge-transfer (LTMCT) bands arising from coordination of low-valent sulfur to a potentially oxidizing center.

Description of Crystal Structure. Atomic positional parameters and their estimated standard deviations for the nonhydrogen atoms as obtained in the last cycle of least-squares refinement are listed in Table II. Those for the hydrogen atoms along with the associated isotropic thermal parameters appear in Table B.[21] Anisotropic thermal parameters for nonhydrogen atoms are given in Table C,[21] the root-mean-square displacements for these atoms are presented in Table III, and the associated ellipsoids may be seen in Figures 1–3. Nonhydrogen atom bond lengths and bond angles may be found in Tables IV and V, respectively. Those involving hydrogen atoms occur in Tables D[21] and E.[21]

The crystal consists of six-coordinate "octahedral" cobalt cations and nitrate anions held together by a rather weak series of hydrogen bonds. The cobalt atom is coordinated by four nitrogen atoms from the two ethylenediamine chelates and by the nitrogen and selenium atoms of the chelating 2-selenolatoethylamine. A ground-state, structural trans effect is apparent in that the trans Co–N distance is 2.034 (2) Å (N(3), trans to Se) and the average cis Co–N distance is 1.971 (9) Å,[23] giving a difference between cis and trans distances of 0.063 (9) Å. This centric crystal contains enantiomers of Δλλδ and Λδδλ configurations where the two ethylenediamine

Table VI. Possible Hydrogen Bonds

	Distances, Å				Angles, deg		Distance out of NO_3 plane, Å	
			H· · ·O					
N–H· · ·O–N′ atoms	N–H	N· · ·O	Found	Cor[d]	N–H· · ·O	H· · ·O–N′	H	N
N(1), H(11), O(5), N(7)	1.01	2.98	1.97	1.98	175	111	0.21	0.27
N(1),[a] H(12),[a] O(2), N(6)	0.85	3.04	2.25	2.12	155	108	0.49	0.91
N(2),[b] H(21),[b] O(5), N(7)	0.97	3.22	2.27	2.24	169	96	0.15	0.37
N(2),[a] H(22),[a] O(1), N(6)	0.82	2.93	2.18	2.02	152	139	0.01	0.39
N(3),[c] H(32),[a] O(6), N(7)	0.98	3.12	2.21	2.19	154	111	0.00	0.41
N(4),[b] H(41),[b] O(3), N(6)	0.85	3.11	2.30	2.16	160	111	1.01	1.57
N(4),[c] H(42),[c] O(4), N(7)	0.81	2.92	2.17	2.00	155	132	0.65	1.15
N(5), H(51), O(3), N(6)	0.91	3.17	2.30	2.22	162	109	0.72	1.12

[a] Transformed to $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. [b] Transformed to $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. [c] Transformed to $\frac{1}{2} - x, -\frac{1}{2} + y, 1\frac{1}{2} - z$. [d] The corrected H· · ·O distance is calculated by positioning the hydrogen atom at 1.00 Å from its bound nitrogen partner and along the line found in the crystal structure for N–H.

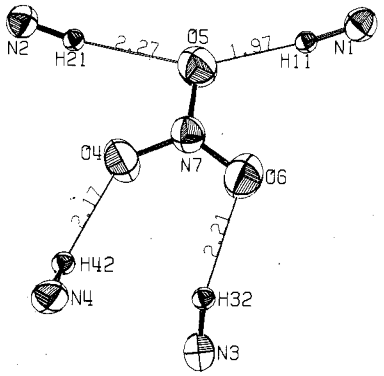

Figure 3. The second nitrate ion showing its hydrogen-bonding network.

chelates adopt alternate conformations as can be observed in Figure 1.

The hydrogen bonds which form between hydrogen atoms of the coordinated amines and the oxygen atoms of the nitrate anions are listed in Table VI and illustrated in Figures 2 and 3. The average value for 12 refined H–C distances is 0.97 Å with individual esd's of 0.02 Å and for 10 determinations of N–H it is 0.88 Å with individual esd's of 0.03 or 0.02 Å. For bond angles involving hydrogen atoms the individual esd's are 1 or 2° and the average values found are as follows: H–N–C, 111° (10 determinations); H–N–Co, 110° (10 determinations); H–N–H, 104° (5 determinations); H–C–C, 111° (12 determinations); H–C–N, 110° (10 determinations); H–C–H, 109° (6 determinations).

Discussion

Preparation and Properties of Complexes. Reduction of bis(2-ammonioethyl) diselenide or diselenodiacetic acid by an ethylenediamine–cobalt(II) mixture according to the procedures used to prepare the analogous sulfur complexes[3a,24] leads directly to the selenolatobis(ethylenediamine)cobalt(III) complexes

$$2Co^{2+} + 5en + (H_3NCH_2CH_2X\text{-})_2{}^{2+} \rightarrow 2(en)_2Co^{III}(XCH_2CH_2NH_2)^{2+} + enH_2{}^{2+} \quad (1)$$

$$2Co^{2+} + 5en + (HOOCCH_2X\text{-})_2 \rightarrow 2(en)_2Co^{III}(XCH_2COO)^{+} + enH_2{}^{2+} \quad (2)$$

where X = S, Se. Overall yields for purified salts are on the order of 30–50%. The success of these preparations indicates substantial generality for this indirect redox route to metastable cobalt(III) complexes which contain reducing ligands (both $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ yield $Co_{aq}{}^{2+}$ upon prolonged heating in aqueous perchloric acid media). It also indicates the possibility of synthesizing selenolatochromium(III) and selenolatoiron(III) complexes analogous to the thiolatochromium(III)[22,25] and thiolatoiron(III)[26] complexes prepared by the chromium(II) and iron(II) reduction of organic disulfides.

Table I gives the visible–uv absorption spectra for analogous thiolato and selenolato bis(ethylenediamine)cobalt(III) complexes. The positions of the visible d–d absorption bands show that coordinated selenols provide a weaker ligand field than the analogous coordinated thiols, a trend which is consistent with the well-established spectrochemical series $I^- < Br^- < Cl^-$. By analogy with the thiolato complexes, the intense uv band exhibited by the selenolato complexes is assigned to be a chalcogen-to-metal charge transfer, and the presence of this band may be taken to be diagnostic for the existence of a metal–chalcogen bond. The positions of the LTMCT bands (see Table I) show that in these systems coordinated selenols are better reductants than the analogous coordinated thiols. This conclusion is consistent with our qualitative observation that $[(en)_2Co(SeCH_2CH_2NH_2)]^{2+}$ thermally decomposes to $Co_{aq}{}^{2+}$ under milder conditions than does $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$.

Structural Implications. Coordination Geometry of Cobalt. In the title complex, the cobalt to nitrogen atom bond lengths for those nitrogen atoms cis to the selenium atom are normal, averaging 1.971 (9) Å which is in the range of distances previously reported[27] for Co–N where N is part of an ethylenediamine-like ligand. The cobalt to nitrogen atom bond length for the group trans to selenium is 2.034 (2) Å which yields a ground-state trans lengthening of 0.063 (9) Å. Since the trans effect for thiolato sulfur is 0.040 (6) Å,[3d] it appears that a selenol causes a greater trans effect than a thiol.

The cobalt to selenium atom bond length (2.378 (1) Å) is apparently the first of this type to be determined. A value of 2.374 Å is predicted based on the analogous sulfur-containing compounds.[28] The sum of the covalent radii for cobalt and selenium[29] is 2.36 Å. A nickel(II) complex of diphenyl-*o*-selenolatophenylphosphine[30] has an Ni–Se distance of 2.280 (3) Å, which when adjusted for the change in covalent radius in going to square-planar nickel (Δ = 0.06 Å), would predict 2.34 Å for the Co–Se distance; however, there is probably a significant shortening of the Ni–Se distance due to multiple bonding. Several other[31–35] metal to selenium bond distances have been determined; however, none of them is closely analogous to the structure reported here.

Ligand and Counterion Geometry. The selenium to carbon atom distance of 1.952 (3) Å compares favorably with the weighted average of 1.964 (27) Å obtained from the 13 aliphatic carbon atom to selenium atom distances listed by Aleby.[36] The remaining ligand bond lengths and angles, reported in Tables IV and V, are as expected. The slight difference observed between the nitrogen to oxygen atom bond lengths in one nitrate, N(6), O(1), O(2), and O(3), compared to that in the other may be ascribed to the larger thermal motion of the former[37] which is evident from Table III and Figures 2 and 3.

Hydrogen Bonding. The effects of hydrogen bonding are of some interest in this structure for two reasons. First, hydrogen bonds have been held responsible for lengthening metal to nitrogen atom bonds.[38] Second, strong hydrogen bonding has been reported to lead to the adoption of an "unfavorable" conformational wrapping of ligands about a central metal ion.[39,40]

The possible hydrogen bonds which are formed between coordinated amine hydrogen atoms and the oxygen atoms of the nitrate anions may be examined to see if they satisfy various[41] criteria: (1) short N···O distance (less than 3.1 Å), (2) short H···O distance (less than 2.6 Å), (3) linear N–H···O array, (4) coplanarity of the N–H fragment with the nitrate ion, (5) H···O–N angle near 120°. Of the possible hydrogen bonds listed in Table VI only that involving N(1), H(11), O(5), and N(7) appears close to satisfying all of these criteria. Two others—N(2), H(22), O(1), N(6) and N(4), H(42), O(4), N(7)—appear to satisfy criteria 1 and 2 but they do not contain a linear N–H···O grouping and the amine group of the latter is far out of the nitrate ion plane, as can be seen in Figure 3. Thus, it seems there are few strong hydrogen bonds present in this crystal. The Co–N(1) distance (1.982 (2) Å) is the longest of the four cis cobalt to nitrogen atom bonds and it may be argued that the two hydrogen bonds involving H(11) and H(12) have lengthened it. More importantly N(3), the amino nitrogen trans to selenium, participates in little, if any, hydrogen bonding. Thus the ground-state trans effect must be ascribed to the cationic complex itself rather than to a hydrogen bonding effect.

In this complex the gauche conformation of each of the three ligands makes possible eight different isomers, $\Delta\lambda\lambda\lambda$, $\Delta\lambda\lambda\delta$, $\Delta\lambda\delta\delta$, and $\Delta\delta\delta\delta$ and their four enantiomers. For $[Co(en)_3]^{3+}$ the $\Delta\lambda\lambda\lambda$ structure is calculated to be the most stable for the isolated cation in agreement with solution equilibrium experiments.[42] The occurrence of the "unfavored" isomers, all of which have been found to occur in various structures,[43] has been postulated to result from an increase in the hydrogen bonding which becomes possible with change of conformation. The configurations $\Delta\lambda\lambda\lambda$ and $\Lambda\delta\delta\delta$ are found for $[Co(en)_2cys](SCN)_2$, the sulfur analogue of this structure, and rather weak hydrogen bonding is present.[3d] However, the hydrogen bonding in the present structure is also minimal and it seems more likely that the $\Delta\lambda\lambda\delta$ and $\Lambda\delta\delta\lambda$ configurations found here are the result of accommodating the larger selenium atom into this structure. Certainly N(4) and N(5), which are in an ob configured ring, form no more or stronger hydrogen bonds than N(2) and N(3), which are in an lel configured one.

Trans Effect. The currently favored[44] view of the origins of trans effects involves both σ and π electronic effects. σ effects are thought to be operative in both d^6 octahedral complexes and d^8 square-planar complexes, whereas metal–ligand π bonding is thought to be of importance[45] only in the d^8 case. Strong σ-donating ligands maximize $S^2/\Delta E$ (where S is the overlap integral between and ΔE the absolute energy separation of the metal and ligand orbitals),[47] which leads to a large influence on the trans bond. Since there are currently no convenient ways to determine the σ-donating ability of ligands[5] or calculate $S^2/\Delta E$ values for fourth-row elements, we must at this time be content with empirical correlations of trans effects. To our knowledge there are no previous quantitative comparisons of the trans effects of sulfur- and selenium-containing ligands in octahedral d^6 complexes, and only one such comparison in square-planar d^8 complexes.[7,44,48] Chatt, Duncanson, and Venanzi[49] measured N–H stretching frequencies, band intensities, and association constants for the series of Pt(II) complexes *trans*-$[L(am)PtCl_2]$ (where am = RNH_2 or R_2NH) and determined the relative trans effect for several uncharged ligands including R_2Te, R_2Se, and R_2S (in order of decreasing trans effect). Wherever comparisons with data obtained subsequently (by a variety of techniques) have been possible, their results for ligands not containing Se and Te have been confirmed.[44b] Thus, it is not unreasonable to accept their relative ordering for the ligands containing group 6 elements. Since the amine ligand in the $[L(am)PtCl_2]$ series can have only minimal π interactions with Pt(II), the ordering observed by Chatt, Duncanson, and Venanzi should be that expected for d^6 octahedral complexes where π interactions do not seem to be important in determining trans effects.[44,45] Thus, our determination in this work that, for analogous Co(III) complexes, RSe^- exerts a greater ground-state trans effect than RS^- is consistent both with the currently accepted view of the origins of trans effects and with the limited data currently available for group 6 ligating atoms. The implications of this determination, with respect to the reactivities of selenolato and thiolato complexes, are currently under investigation.

Acknowledgment. Financial support by the National Science Foundation, Grant No. MPS74-01540 A01, and the Research Council of the University of Cincinnati is gratefully acknowledged.

Registry No. $[(en)_2Co(SeCH_2CH_2NH_2)](ClO_4)_2$, 58866-02-7; $[(en)_2Co(SeCH_2CH_2NH_2)](S_2O_3)$, 58866-03-8; $[(en)_2Co(SeCH_2CH_2NH_2)](NO_3)_2$, 58881-37-1; $[(en)_2Co(SeCH_2COO)](ClO_4)$, 58866-05-0; $(H_3NCH_2CH_2Se-)_2[SO_4]$, 2885-43-0; ethylenediamine, 107-15-3.

Supplementary Material Available: Tables A–E, listing structure factor amplitudes, H atom positional parameters, anisotropic thermal parameters of nonhydrogen atoms, H–X bond lengths, and bond angles involving hydrogen (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) For recent reviews of selenium biochemistry see (a) T. C. Stadtman, *Science*, **183**, 915 (1974); (b) H. E. Ganther in "Selenium", R. A. Zingaro and W. C. Cooper, Ed., Reinhold, New York, N.Y., 1974, Chapter 9; (c) "Organic Selenium Compounds: Their Chemistry and Biology", D. L. Klayman and W. H. H. Gunther, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter XIII; (d) R. Walter, I. L. Schwartz, and J. Roy, *Ann. N.Y. Acad. Sci.*, **192**, 175 (1972).

(2) (a) O. A. Levander, V. C. Morris, and D. J. Higgs, *Biochemistry*, **12**, 4591 (1973); (b) O. A. Levander, V. C. Morris, and D. J. Higgs, *ibid.*, **12**, 4586 (1973); (c) R. L. Lester and J. A. DeMoss, *J. Bacteriol.*, **105**, 1006 1971; (d) P. D. Whanger, N. D. Pedersen, and P. H. Weswig, *Biochem. Biophys. Res. Commun.*, **53**, 1031 (1973); (e) K. Mukai, J. J. Huang and T. Kimura, *ibid.*, **50**, 105 (1973); (f) E. Munck, P. G. Debrunner, J. C. M. Tsibris, and I. C. Gunsalus, *Biochemistry*, **11**, 885 (1972).

(3) (a) R. H. Lane and L. E. Bennett, *J. Am. Chem. Soc.*, **92**, 1089 (1970); (b) C. J. Weschler, J. C. Sullivan, and E. Deutsch, *ibid.*, **95**, 2720 (1973); (c) C. J. Weschler, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **13**, 2360 (1974); (d) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *ibid.*, **12**, 2690 (1973). (e) M. Woods, J. C. Sullivan, and E. Deutsch, *J. Chem. Soc., Chem. Commun.*, 749 (1975); (f) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **15**, 139 (1976).

(4) R. C. Elder and M. Trkula, *J. Am. Chem. Soc.*, **96**, 2635 (1974).

(5) J. M. Palmer and E. Deutsch, *Inorg. Chem.*, **14**, 17 (1975).

(6) A poorly defined, uncharacterized material formulated as $Co(SeCH_2CH_2NH_2)_3$ has been reported: H. Sakurai, A. Yokoyama, and H. Tanaka, *Chem. Pharm. Bull.*, **19**, 1270 (1971).

(7) For recent reviews of coordination compounds in which selenium functions as a donor atom see (a) V. Krishman and R. A. Zingaro in "Selenium", R. A. Zingaro and W. C. Cooper, Ed., Reinhold, New York, N.Y., 1974, Chapter 7; (b) K. A. Jensen and C. K. Jorgensen in "Organic Selenium Compounds: Their Chemistry and Biology", K. L. Klayman and W. H. H. Gunther, Ed., Wiley-Interscience, New York, N.Y., Chapter XVI.

(8) D. L. Klayman, *J. Org. Chem.*, **30**, 2454 (1965).

(9) W. H. H. Gunther, *J. Org. Chem.*, **32**, 3929 (1967).

(10) D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **95**, 197 (1973).

(11) H. J. Backer and W. Van Dam, *Recl. Trav. Chim. Pays-Bas*, **49**, 482 (1930).

(12) "International Tables for X-Ray Crystallography", Vol. 1, 2d ed, Kynoch Press, Birmingham, England, 1965. The choice of the less usual $P2_1/n$ space group over the standard $P2_1/c$ leads to a β angle closer to 90°.

(13) R. M. Wilson, E. J. Gardner, R. C. Elder, R. H. Squire, and L. R. Florian, *J. Am. Chem. Soc.*, **95**, 2955 (1974).
(14) R. C. Elder and M. Trkula, to be submitted for publication.
(15) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(16) All computations were performed using a local version of X-RAY 67: J. M. Stewart, University of Maryland, crystallographic computer system.
(17) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, where R_1 and R_2 are calculated using observed reflections only; $R_3 = R_1$ for "unobserved" reflections ($I < 2\sigma(I)$).
(18) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(19) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(20) "International Tables for X-Ray Crystallography", Vol. 3, Kynoch Press, Birmingham, England, p 215.
(21) Supplementary material.
(22) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **12**, 2682 (1973), and references therein.
(23) The error in the average distance has been computed using $\sigma_{\bar{d}} = [\sum(d_i - \bar{d})^2/(n - 1)]^{1/2}$. The error in the difference is computed according to $\sigma_\Delta = [\sigma^2_{\mathrm{cis}} + \sigma^2_{\mathrm{trans}}]^{1/2}$.
(24) L. Asher and E. Deutsch, *Inorg. Chem.*, **12**, 1774 (1973).
(25) L. Asher and E. Deutsch, *Inorg. Chem.*, **11**, 2927 (1972).
(26) S. Koch, S. C. Tang, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **97**, 914 (1975).
(27) See ref 3d and references therein.
(28) The value of 2.374 Å is obtained as follows. The average Co–S distance from the two cobalt–thiolate structures (2.235 Å)[3d] is increased by the change in radius on going from sulfur to selenium. The latter is computed as the difference (0.139 Å) in the C–Se bond (1.952 Å) and the average of three C–S bonds (1.813 Å).[3d]
(29) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, Chapter 7.
(30) R. Curran, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 2749 (1970).
(31) For tris[*cis*-1,2-bis(trifluoromethyl)ethylene-1,2-diselenato]molybdenum, $Mo[Se_2C_2(CF_3)_2]_3$, Mo–Se = 2.492 (2) Å: C. G. Pierpoint and R. Eisenberg, *J. Chem. Soc. A*, 2285 (1971).
(32) For nickel diethyldiselenocarbamate, $Ni[Se_2CN(C_2H_5)_2]_2$, Ni–Se = 2.317 (1) Å (as corrected in ref 31): M. Bonamico and G. Dessy, *Chem. Commun.*, 1114 (1967).
(33) For bis{μ-[(trifluoromethyl)seleno]-manganese tetracarbonyl}, $[(CF_3Se)Mn(CO)_4]_2$, Mn–Se = 2.498 (6) Å: C. J. Marsden and G. M. Sheldrick, *J. Organomet. Chem.*, **40**, 175 (1972).
(34) For bis(*N,N*-diethyldiselenocarbamato)dioxo(triphenylarsine oxide)uranium(VI), $UO_2[Se_2CN(C_2H_5)_2]_2Ph_3AsO$, U–Se = 2.98 Å: B. Zarli, R. Graziani, E. Forsellini, V. Croatto, and G. Bombieri, *Chem. Commun.*, 1501 (1971).
(35) For the palladium(II) chloride complex with 1,2-bis(isopropylseleno)ethane, $(i\text{-}C_3H_7SeC_2H_4Se\text{-}i\text{-}C_3H_7)PdCl_2$, Pd–Se = 2.38 (2) Å: H. J. Whitfield, *J. Chem. Soc. A*, 113 (1970). This distance is suspiciously short when compared to the sum of the covalent radii, 2.46 Å.
(36) S. Aleby, *Acta Crystallogr., Sect. B*, **28**, 1509 (1972).
(37) R. C. Elder, *Inorg. Chem.*, **13**, 1037 (1974).
(38) G. G. Messmer and E. L. Amma, *Acta Crystallogr., Sect. B*, **24**, 417 (1968).
(39) K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, **7**, 2333 (1968).
(40) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 597 (1972).
(41) M. D. Joesten and L. J. Schaad, "Hydrogen Bonding", Marcel Dekker, New York, N.Y., 1974, pp 35–40.
(42) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, N.Y., 1971, pp 75–82.
(43) Reference 39 and references therein.
(44) For recent reviews of trans effects see (a) F. R. Hartley, *Chem. Soc. Rev.*, **2**, 163 (1973); (b) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 355 (1973); (c) J. M. Pratt and R. G. Thorp, *Adv. Inorg. Chem. Radiochem.*, **12**, 375 (1969).
(45) A synergistic effect in which a π bond between the trans-influencing ligand and the metal atom strengthens the σ bond of the trans-influencing ligand and increases $S^2/\Delta E$ is of course still possible.[46] However, for convenience we still classify this as a σ effect in that the trans bond is a purely σ interaction.
(46) (a) W. R. Scheidt, *Inorg. Chem.*, **12**, 1758 (1973); (b) W. R. Scheidt et al., *J. Am. Chem. Soc.*, **93**, 3867, 3873, 3878 (1971).
(47) R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970).
(48) S. E. Livingstone, *Q. Rev., Chem. Soc.*, **19**, 386 (1965).
(49) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Crystal and Molecular Structure of *trans*-μ-Dichloro-bis(phenylazophenyl-2*C*,*N'*)diplatinum(II)[1]

R. C. ELDER,* R. D. "PETE" CRUEA, and ROXANE FLORIAN MORRISON

Received January 21, 1976 AIC60051E

The crystal structure of *trans*-μ-dichloro-bis(phenylazophenyl-2*C*,*N'*)diplatinum(II), $[(C_{12}H_9N_2)PtCl]_2$, has been determined by x-ray diffraction techniques. The compound crystallizes in the monoclinic system, space group $C2/c$, with a = 27.07 (3) Å, b = 4.087 (3) Å, c = 20.91 (2) Å, β = 106.46 (8)°, and Z = 4. Halves of the dimeric molecule are related by a center of symmetry. Each platinum atom is coordinated to the two bridging chloride ions, an ortho carbon atom of a phenyl ring, and the distant azo nitrogen atom such that the azobenzene ligand forms a five-membered chelate. The entire molecule is planar with the exception of the free phenyl rings which are twisted 39° about the C–N bond away from the bridging chloride ions. The σ bond between the aromatic carbon and platinum atoms causes a significant lengthening (0.134 (8)° Å) of the trans Pt–Cl distance.

Introduction

Since the original reports[2,3] of the ortho metalation of azobenzene, there has been considerable interest[4–6] in ortho-metalation reactions. From the original studies involving nitrogen donor atoms in the ortho-metalated ligand, interest has spread to ligands with sulfide,[7] thioester,[8] and phosphite[9] donor groups among others and to complexes in which the ortho-metalated complex contains a six-membered chelate ring.[10] Weaver[11] established by x-ray methods that a σ bond is formed between the ortho carbon atom of azobenzene and palladium. Hoare and Mills[12,13] showed further by x-ray studies that azobenzene forms a five-membered chelate ring in rhodium complexes. Doedens[14] and co-workers have recently added to their series of structures in this field that of a possible intermediate in the ortho palladation of azobenzene. However, due partly to the difficulty in obtaining suitable crystals, the structure of the original Cope and Siekman product, μ-dichloro-bis(phenylazophenyl-2*C*,N')diplatinum(II), has not been reported until now.

Experimental Section

The title compound was prepared as previously described[2] and was recrystallized with some difficulty from tetrahydrofuran solution. Saturated solutions of the complex were prepared at room temperature and filtered into test tubes which then were tightly stoppered with corks. After 1 week the solutions had evaporated by diffusion through the cork to approximately one-fourth the original volume and a few small, needle-shaped single crystals were found in several of the test tubes. One of the largest single crystals (approximate dimensions 0.6 × 0.1 × 0.05 mm, mounted along the needle axis, coincident with b) was used for precession photographs and subsequent intensity measurements. Systematic absences determined from both photo-