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Structural Characterization of Crystalline Tetrakis(2-aminoethanethiol)trinickel(II) Chloride, $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$. A New Basic Trinuclear Metal System Containing Nickel(II)–Nickel(II) Interactions[1]

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A structural determination of the Busch–Jicha complex $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$ has revealed the detailed stereochemical nature of a new basic trinuclear metal system for the divalent tetrakis(2-aminoethanethiol)trinickel(II) cation. The framework of the diamagnetic cation may be seen as arising from the chelation of two identical $Ni(NH_2CH_2CH_2S)_2$ entities of *cis* configuration to a third nickel(II) atom by four Ni–S bonds such that this central nickel(II) is surrounded by four planar bridging sulfur atoms. The steric requirements of the chelating $NH_2CH_2CH_2S$ ligands necessitate that the fusion of the central planar NiS_4 unit with each of the two essentially planar NiN_2S_2 units along the S–S line give rise to a nonplanar fragment of torsional angle 109°. The resulting $Ni\{NiN_2S_2\}_2$ entity ideally possesses a chair conformation of C_{2h}-$2/m$ symmetry. Inclusion of the methylene groups to produce the observed conformation of the entire cation lowers the symmetry to the crystallographically observed C_i-$\bar{1}$. The prime structural feature is the short Ni(II)–Ni(II) distance of 2.733 (7) Å found in the symmetrical linear array of three nickel atoms. A qualitative MO bonding description was invoked in order to rationalize the possible existence of a *weak* metal–metal bonding stabilization originating from the $3d_{z^2}$ and $4p_z$ orbital interactions of the trinickel system. The ionic compound forms triclinic crystals with one formula unit in a centrosymmetric primitive unit cell with parameters $a = 5.29 \pm 0.01$ Å, $b = 8.55 \pm 0.015$ Å, $c = 11.19 \pm 0.02$ Å, $\alpha = 110° 28' \pm 10'$, $\beta = 96° 32' \pm 10'$, and $\gamma = 91° 50' \pm 10'$. The structure (including all hydrogen atoms) was solved by three-dimensional Patterson and Fourier methods and refined by the full-matrix least-squares method to $R_1(F) = 4.9\%$ and $R_2(F) = 5.4\%$, based on 1213 independent intensity maxima obtained photographically. The crystal structure was shown to be partially stabilized by a hydrogen-bonding network involving the amine groups of the cations and the chloride anions.

The diverse stereochemical behavior of the biologically important mercaptan group as a donor in the formation of a large variety of transition metal–sulfur complexes makes this ligand particularly interesting. Chemical and physical investigations of such complexes derived from mercaptide ions or polydentate ligands containing the mercapto ligand have demonstrated mercaptan's widespread tendency to bridge transition metals.[3] The complete range of possible linkages of the mercapto ligand to transition metals in organometallic carbonyl and cyclopentadienyl complexes has been revealed from structurally proven examples showing SR ligands attached to one,[4] two,[5] and three[6] transition metal atoms by formal use of one, three, and all five of its available valence electrons.

From the reaction of 2-aminoethanethiol with nickel(II) chloride in aqueous solution Jicha and Busch[7] isolated a solid trinuclear nickel complex of composition $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$. The existence of this type of trinuclear metal complex in aqueous solution was established from spectrophotometric continuous-variation investigations. The ionic nature of the compound as a 2–1 electrolyte was demonstrated from conductivity studies. From the compound's diamagnetic character at room temperature, determined from magnetic measurements by the Gouy method, Jicha and Busch[7] concluded that all three nickel(II) atoms possess planar coordination. The fact that this trinuclear nickel complex can also be readily synthesized as the result of the solubilization of the neutral *cis* complex bis(2-aminoethanethiol)nickel(II), $Ni(NH_2CH_2CH_2S)_2$, by nickel(II) chloride led them to postulate[7] a structure for $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2{}^{2+}$ that involved the bonding of the third nickel(II) atom with an unshared electron pair from each of the four sulfur atoms in two *cis*-$Ni(NH_2CH_2CH_2S)_2$ molecules. They further predicted a chair conformation for this cation,[7] since the presumed tetrahedral-like nature of the four valence orbitals of each bridged sulfur atom would preclude coplanarity for the coordinated groups of two adjacent nickel(II) atoms.

Jicha and Busch[7] also prepared the corresponding diamagnetic trinuclear palladium(II) derivative and a paramagnetic cobalt(II) trimer of identical formula. They[8] extended this trinuclear metal series to include heterometallic cations of formulas $M'\{Ni(NH_2CH_2CH_2S)_2\}_2{}^{n+}$ (where M′ = Cu(II), Cu(I), Pd(II), Pt(II), and Cd(II)) and $Ni\{Pd(NH_2CH_2CH_2S)_2\}_2{}^{2+}$ and suggested that the copper(I) and cadmium(II) form

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[2] (a) University of Wisconsin and the Oak Ridge National Laboratory. (b) University of Wisconsin.

[3] L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969), and references cited therein.

[4] *Cf.*: (a) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 482 (1965); (b) S. A. Giddings, Abstracts of Proceedings, 2nd International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965, p 121; (c) S. F. Watkins and L. F. Dahl, submitted for publication, and references contained therein.

[5] (a) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963); (b) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **90**, 3960 (1968), and references cited therein.

[6] C. H. Wei and L. F. Dahl, *ibid.*, **90**, 3969, 3977 (1968).

[7] D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).

[8] D. C. Jicha and D. H. Busch, *ibid.*, **1**, 878 (1962).

trimetal adducts by tetrahedral coordination with the four sulfur atoms of the two *cis*-$Ni(NH_2CH_2CH_2S)_2$ molecules. A recent comprehensive study by Root and Busch[9] of the various nickel(II) complexes obtained from a number of N-monosubstituted and N,N-disubstituted 2-aminoethanethiols showed that trinuclear nickel(II) cations could be isolated only when the steric repulsion requirements of the ligand were relatively limited. Wrathall and Busch[10] found that the ligand 2-(2-mercaptoethyl)pyridine could also be utilized to synthesize analogous sulfur-bridged homometallic cations with nickel(II) and palladium(II), as well as the heterometallic $Ni\{Pd(NC_5H_4CH_2CH_2S)_2\}_2^{2+}$ and $Co\{Ni(NC_5H_4CH_2CH_2S)_2\}_2^{2+}$ cations.

Structural analysis of $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$ by the single-crystal X-ray diffraction method was carried out to provide detailed stereochemical information on the nature of this sulfur-bridged trimetal system and to determine the various factors which contribute to the stabilization of these trinuclear metal complexes. This investigation revealed that the molecular architecture of the cation possesses short nickel–nickel distances indicative of direct nickel(II)–nickel(II) interactions.

Experimental Section

Black needle crystals of $[Ni\{Ni(NH_2CH_2CH_2S_2)\}_2]Cl_2$, generously supplied by Professor D. H. Busch and Dr. D. C. Jicha of The Ohio State University, were used for our X-ray study without further recrystallization. A cylindrically shaped single crystal of length 0.77 mm and diameter 0.12 mm was selected for the collection of Weissenberg data, while another cylindrically shaped crystal of length 0.59 mm and diameter 0.05 mm was used for obtaining precession data. Both crystals were mounted in thin-walled glass capillaries along their needle axes, which corresponded to the *a* axis of the chosen triclinic unit cell. Unit cell parameters were determined at room temperature (24°) from both Weissenberg and precession photographs, with the estimated errors based on reproducibility of the measurements. Multiple-film equiinclination Weissenberg data were obtained with zirconium-filtered Mo Kα radiation (λ 0.7107 Å) for reciprocal levels $0kl$ through $6kl$. To minimize errors due to spot compaction,[11] a full 360° range of Weissenberg data consisting of two separate sets of film packets was taken for each nonzero reciprocal lattice level, and the intensities of only the reflections recorded on the top halves of the films were measured. Timed-exposure precession photographs of $h0l$, $h1l$, and $hk0$ zones were collected with zirconium-filtered Mo Kα radiation from the second crystal. All intensities were estimated visually by comparison with corresponding sets of standard spots and then corrected for Lorentz and polarization effects. No corrections were made for absorption or extinction. With the linear absorption coefficient having a μ value of 36.4 cm^{-1} for Mo Kα radiation, the maximum intensity variation on a given reciprocal layer due to absorption was estimated to be less than 10%. All 1213 independent, observed reflections (obtained from the 10 Weissenberg and precession reciprocal levels) were merged to put them on an initial relative common scale;[12] the separate reciprocal level scale factors were subsequently refined by least squares. Minimum observed intensities, I_o(min), were estimated for each reciprocal level, and variable weights were assigned to individual observed reflections according to the following scheme: $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o$(min); $\sqrt{w} = 1.25I_o^2/F_oI_o^2$(min) if $I_o < 4I_o$(min).

Results

Crystal Data.—The reduced primitive triclinic unit cell of symmetry $P\bar{1}$ (C_i^1, no. 2) and cell parameters $a = 5.29 \pm 0.01$ Å, $b = 8.55 \pm 0.015$ Å, $c = 11.19 \pm 0.02$ Å, $\alpha = 110° 28' \pm 10'$, $\beta = 96° 32' \pm 10'$, and $\gamma = 91° 50' \pm 10'$ contains one formula unit of $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$. The volume of the unit cell is 470 Å^3. The observed density of 1.94 ± 0.02 g cm^{-3} (obtained from the flotation method) is in satisfactory agreement with the calculated value of 1.95 g cm^{-3}. The total number of electrons per cell, $F(000)$, is 282.

Determination of the Structure.—A three-dimensional Patterson function was calculated[13] from the observed structure factor amplitudes. From an inspection of this function with due regard to expected interatomic distances, trial positional parameters for two nickel, one chlorine, and two sulfur atoms were found which conformed to the centrosymmetric space group $P\bar{1}$. This choice of space group was subsequently corroborated by the satisfactory least-squares refinement of the structure. Determination of the structure involved the location of 2 nickel, 2 sulfur, 2 nitrogen, 4 carbon, 1 chlorine, and 12 hydrogen atoms. One nickel atom was conveniently chosen to lie on the particular crystallographic center of symmetry that corresponded to the special position (1h): $^1/_2$, $^1/_2$, $^1/_2$; all of the other crystallographically independent atoms occupy the general twofold set of positions (2i): $\pm(x, y, z)$.[14] A block-diagonal least-squares refinement[15] of positional parameters and individual atom isotropic temperature factors for the five heavy atoms together with the ten reciprocal level scale factors was carried out. Isotropic temperature factors of 2.0 Å^2 for each nickel atom and 3.0 Å^2 for each sulfur and chlorine atom were initially assigned. After two cycles the unweighted discrepancy index, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$, had a value of 18.2%. A three-dimensional Fourier synthesis[13] phased on these nickel, chlorine, and sulfur atoms unambiguously revealed the positions of the other six crystallographically independent nonhydrogen atoms, the distinction between carbon and nitrogen atoms being made on the basis of chemical knowledge. Further block-diagonal least-squares refinement of the positional and thermal parameters for the 11 nonhydrogen atoms, in which initial isotropic thermal parameters for each nitrogen and carbon atom were arbitrarily chosen to be 5.0 Å^2, lowered the R_1 value to 7.9%, after which the Busing–Martin–Levy full-matrix least-squares program[16] was used to obtain the standard errors from the full inverse

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[9] C. A. Root and D. H. Busch, *Inorg. Chem.*, **7**, 789 (1968).

[10] J. W. Wrathall and D. H. Busch, *ibid.*, **2**, 1182 (1963).

[11] *Cf.* M. J. Buerger, "X-Ray Crystallography," Wiley, New York, N. Y., 1942, pp 227–229.

[12] Of the common Weissenberg and precession reflections, only the Weissenberg ones were used in the least-squares refinements.

[13] J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, Madison, Wis., 1965.

[14] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 75.

[15] P. W. Sutton, "A Crystallographic Block-Diagonal Least-Squares Program for the CDC 1604 Computer," University of Wisconsin, 1962.

[16] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

TABLE I

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS (10^4) FOR NONHYDROGEN ATOMS[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	0.5000	0.5000	0.5000	269 (4)	107 (2)	61 (1)	22 (3)	14 (2)	35 (2)
Ni(2)	0.4087 (2)	0.2422 (1)	0.2681 (1)	259 (3)	115 (2)	63 (1)	8 (2)	13 (1)	28 (1)
S(1)	0.1630 (3)	0.4365 (3)	0.3506 (2)	275 (6)	151 (4)	72 (2)	28 (4)	23 (3)	45 (2)
S(2)	0.4574 (3)	0.2270 (2)	0.4576 (2)	275 (6)	125 (4)	81 (2)	10 (4)	25 (3)	48 (2)
Cl	0.1653 (4)	−0.1742 (3)	0.0565 (2)	378 (7)	195 (5)	99 (2)	44 (5)	25 (3)	45 (3)
N(1)	0.3823 (12)	0.3015 (9)	0.1187 (6)	316 (21)	213 (15)	65 (7)	56 (15)	28 (10)	35 (8)
N(2)	0.6530 (13)	0.0779 (9)	0.2143 (7)	411 (26)	150 (13)	76 (7)	84 (15)	49 (11)	35 (8)
C(1)	0.3824 (16)	0.4868 (13)	0.1552 (9)	406 (31)	232 (21)	111 (11)	89 (20)	65 (15)	87 (13)
C(2)	0.1727 (16)	0.5453 (12)	0.2364 (8)	449 (32)	197 (18)	84 (9)	64 (20)	29 (14)	60 (11)
C(3)	0.7440 (17)	0.0024 (11)	0.3096 (9)	463 (34)	148 (16)	131 (11)	35 (20)	57 (16)	43 (11)
C(4)	0.7636 (13)	0.1307 (11)	0.4439 (8)	284 (24)	151 (15)	95 (9)	42 (16)	38 (12)	42 (10)

[a] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Standard deviations of the last significant figures are given in parentheses here and in succeeding tables.

matrix (with inclusion of the estimated unit cell uncertainties).

TABLE II

HYDROGEN POSITIONAL PARAMETERS

Atom	x	y	z
H(1)	0.256 (21)	0.257 (14)	0.033 (11)
H(2)	0.496 (21)	0.254 (13)	0.040 (11)
H(3)	0.352 (20)	0.506 (14)	0.076 (10)
H(4)	0.524 (22)	0.572 (15)	0.225 (10)
H(5)	0.141 (20)	0.688 (14)	0.279 (10)
H(6)	0.015 (21)	0.507 (13)	0.169 (10)
H(7)	0.564 (20)	−0.015 (14)	0.131 (11)
H(8)	0.797 (22)	0.131 (14)	0.194 (10)
H(9)	0.930 (20)	−0.059 (13)	0.273 (10)
H(10)	0.624 (20)	−0.094 (14)	0.308 (10)
H(11)	0.774 (20)	0.040 (14)	0.514 (10)
H(12)	0.894 (20)	0.220 (14)	0.465 (10)

Four cycles of isotropic full-matrix least-squares, refinement resulted in an R_1 value of 6.1% and a value of the weighted discrepancy index, $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$, of 7.1%. All parameter shifts in the last cycle were negligible compared to the corresponding standard deviations. A three-dimensional difference Fourier map, computed[13] on the basis of these refined parameters, showed 32 positive peaks whose densities ranged from 0.3 to 0.8 e$^-$/Å^3; the minimum density on the map was −0.6 e$^-$/Å^3. Although some of the 32 peaks were in the neighborhood of nickel and sulfur atom positions, 12 peaks were in chemically reasonable positions for the 12 hydrogen atoms attached to the carbon and nitrogen atoms. To obtain more reliable hydrogen atomic positions, least-squares refinement with anisotropic thermal coefficients for all nonhydrogen atoms was then carried out with one scale factor;[17] the R_1 and R_2 values decreased to 5.4 and 6.1%, respectively. Another difference Fourier synthesis showed essentially the same 12 hydrogen positions obtained previously. Therefore, the full-matrix least-squares refinement was continued, with nonhydrogen atoms and hydrogen atoms assigned anisotropic and isotropic thermal parameters, respectively. Although attempts to refine isotropic thermal parameters of hydrogen atoms as well as their positional parameters resulted in reasonably low discrepancy indexes of $R_1 = 4.9\%$ and $R_2 = 5.3\%$, the 12 C–H and N–H distances nevertheless ranged from 0.91 to 1.44 Å. Hence, a reasonable isotropic temperature factor of 5.5 Å^2 was fixed[18] for each hydrogen atom, and hydrogen atom positions were refined together with the positional and anisotropic thermal parameters for the nonhydrogen atoms. After five cycles the R_1 and R_2 values remained at 4.9 and 5.4%, respectively. The parameter shifts for the nonhydrogen atoms were all less than 18% of the corresponding standard deviations, whereas the maximum shift in hydrogen positional parameters was 95% of the corresponding standard deviation. All least-squares refinements were based on the minimization of $\Sigma w|\Delta|F||^2$, and the weights were assigned as previously outlined. The standard deviation of an observation of unit weight, defined as $[\Sigma w|\Delta|F||^2/(n-p)]^{1/2}$ where n is the number of observations and p the number of parameters fitted to the data set, was 0.92. The scattering factors used were those of Thomas and Umeda[19] for the neutral nickel atom,[20] those of Dawson[21] for sulfur and the chloride ion, those of Berghuis, *et al.*,[22] for carbon and nitrogen, and those tabulated by Ibers[23] for hydrogen. No correction for anomalous dispersion effects was made.[24-26] The atomic parameters for nonhydrogen atoms and the positional parameters for hydrogen

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(17) The isotropic refinement with all nonhydrogen atoms resulted in the values ranging from 0.276 to 0.305 for the 10 scale factors. These values were utilized to put all intensity data on one scale prior to the anisotropic refinement.

(18) Temperature factors of nonhydrogen atoms at the end of isotropic refinement ranged from 2.7 Å^2 for the nickel at the special position to 4.9 Å^2 for a carbon atom. Although the temperature factor of 5.5 Å^2 assumed for each hydrogen atom is somewhat larger than the corresponding value for the carbon or nitrogen atoms, the resulting molecular parameters were substantially the same when different fixed isotropic thermal values of 4.5 and 6.5 Å^2 were assumed for each hydrogen atom: *Cf.* E. O. Schlemper, *Inorg. Chem.*, **7**, 1130 (1968).

(19) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(20) As expected, a comparison of the atomic contributions of neutral, singly ionized positive,[19] and doubly ionized positive[19] nickel atoms to the calculated structure factors in the last least-squares refinement showed no significant differences in the resulting atomic parameters in these three cases.

(21) B. Dawson, *Acta Crystallogr.*, **13**, 403 (1960).

(22) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(23) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202, Tables 3.3.1A.

(24) The relatively small values of the real and imaginary dispersion corrections for Mo Kα radiation (*i.e.*, $\Delta f' = 0.4$, $\Delta f'' = 1.2$ for Ni; $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for both Cl and S)[25] were presumed not to have any significant effect on the atomic coordinates of this centrosymmetric crystal.[26]

(25) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

(26) D. H. Templeton, *Acta Crystallogr.*, **8**, 842 (1955).

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) FOR $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$

K	L	FO	FC
**** H = 0 ****			
0	2	88	89
0	3	93	98
0	4	519	541
0	5	458	439
0	7	106	93
0	8	132	140
0	9	142	139
0	10	164	170
0	11	87	82
0	13	123	118
1	2	316	330
1	3	413	398
1	-3	129	112
1	4	220	238
1	-4	136	142
1	5	106	98
1	-5	378	381
1	6	132	131
1	-6	683	771
1	7	287	280
1	-7	88	81
1	8	214	221
1	-8	257	261
1	9	125	123
1	-9	227	237
1	10	102	89
1	-10	141	140
1	12	215	212
1	-14	113	101
2	0	242	218
2	1	183	173
2	-1	263	262
2	2	165	148
2	-2	55	65
2	3	82	102
2	-3	441	484
2	4	76	77
2	-4	726	744
2	-5	352	330
2	6	524	532
2	-6	412	401
2	7	261	276
2	-7	450	463
2	-8	91	85
2	9	98	84
2	10	126	118
2	-10	175	194
2	11	182	184
2	-11	183	172
2	-12	116	116
2	-14	141	129
2	-15	142	124
3	0	599	644
3	1	451	408
3	-1	110	108
3	2	319	308
3	-2	403	407
3	3	94	106
3	-3	465	482
3	4	214	210
3	-4	318	273
3	5	465	460
3	-5	442	420
3	6	336	336
3	-6	401	380
3	-7	406	391
3	8	106	109
3	-8	217	222
3	9	150	163
3	-10	244	261
3	-12	111	114
3	-16	110	85
4	0	604	637
4	1	237	238
4	-1	379	376
4	2	435	420
4	-2	286	290
4	3	145	136
4	-3	172	152
4	4	289	286
4	-4	503	550
4	5	337	335
4	-5	229	221
4	6	98	94
4	-6	173	166
4	7	95	93
4	-8	299	324
4	-9	323	328
4	-11	138	140
5	1	342	322
5	-1	448	450
5	-2	219	213
5	3	287	273
5	-3	248	240
5	4	151	151
5	-4	165	157
5	5	123	115
5	-5	264	250
5	-6	259	241
5	-7	96	96
5	-8	135	140
5	-9	238	227
5	-10	366	375
5	-14	137	148
6	0	137	129
6	-1	110	116
6	2	296	302
6	-2	331	344
6	-3	281	283
6	-4	191	182
6	5	128	126
6	-5	150	148
6	6	160	157
6	-6	98	80
6	-7	192	191
6	-9	94	84
6	-10	118	112
6	-11	218	224
6	-15	131	116
6	-16	109	106
7	0	119	112
7	1	256	263
7	-1	89	71
7	2	95	80
7	-2	110	90
7	-3	322	340
7	4	108	110
7	-4	312	324
7	5	183	210
7	-5	224	222
7	-6	151	155
8	0	120	130
8	-1	211	209
8	-3	149	139
8	4	142	135
8	-4	274	273
8	-5	283	301
8	-7	98	83
8	-8	93	101
8	-9	190	202
8	-10	135	132
9	1	115	112
9	-1	113	115
9	3	99	90
9	-4	156	156
9	-6	148	152
9	-5	166	151
9	-10	209	213
9	-11	118	119
10	2	129	112
10	-11	133	138
11	1	124	107
11	-3	121	125
11	-4	116	109
**** H = 1 ****			
0	0	845	828
0	-1	1161	980
0	-2	114	116
0	3	374	382
0	-3	637	635
0	4	868	826
0	-4	184	186
0	5	227	208
0	-5	518	479
0	-6	85	73
0	7	94	106
0	-7	233	228
0	8	208	215
0	-8	177	168
0	-9	307	304
0	-10	154	146
0	-11	164	163
-1	0	248	251
1	1	1189	1130
1	-1	918	855
-1	1	383	346
-1	-1	157	168
1	2	493	462
1	-2	789	922
-1	2	192	199
-1	-2	238	247
1	3	504	456
1	-3	173	179
-1	3	253	256
-1	-3	234	221
1	4	105	113
1	-4	135	135
-1	4	105	105
-1	-4	272	284
1	5	199	210
1	-5	374	384
-1	5	1014	971
-1	-5	252	264
1	6	103	95
1	-6	400	397
-1	6	368	378
-1	-6	164	164
1	7	215	206
1	-7	189	187
-1	7	142	146
1	8	105	89
-1	-8	376	393
1	-9	329	342
-1	9	216	220
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-5	7	150	152
-5	8	110	114
-5	9	180	110
5	-11	199	183
5	-12	156	149
-6	0	104	98
6	1	177	187
-6	1	178	183
6	-2	149	139
-6	-2	144	145
-6	3	211	206
6	4	104	103
6	-4	174	169
6	-5	96	88
-6	5	163	154
6	-6	110	101
-6	6	163	159
-6	9	114	112
7	0	136	132
7	-1	122	117
-7	1	135	128
-7	2	133	133
-7	-2	105	112
7	-4	122	110
-7	4	206	206
7	-5	246	242
-7	-6	146	127
-8	0	148	129
-8	-1	112	106
-8	2	135	130
-8	3	143	130
8	-6	202	194
8	-7	100	97
-8	7	132	135
-9	4	137	129
-9	8	152	157
-9	9	113	113
**** H = 5 ****			
0	0	129	145
0	1	116	123
0	2	174	185
0	-2	214	220
0	3	178	182
0	-3	57	64
0	4	116	109
0	-4	116	123
0	5	100	88
0	-5	95	97
0	-6	241	244
0	-7	76	91
0	-10	136	119
0	-11	145	122
1	0	76	74
-1	0	138	156
1	1	216	227
1	-1	149	156
1	2	116	117
-1	2	142	147
-1	-2	117	133
1	3	93	88
1	-3	184	189
-1	3	185	205
-1	4	208	226
-1	-4	134	137
-1	-5	199	204
-1	6	127	110
-1	-6	73	79
1	-7	176	159
1	-8	82	82
-1	-8	141	126
1	-11	102	84
1	-12	170	138
2	0	276	260
-2	0	70	67
2	1	132	118
2	-1	77	68
-2	1	125	130
2	-2	129	140
-2	-2	162	178
2	-3	69	65
-2	-3	109	112
2	4	126	116
2	-4	153	148
-2	4	240	235
-2	-4	124	133
2	-5	151	148
-2	5	142	143
-2	-5	93	87
2	-6	103	92
-2	-6	161	151
-2	-7	97	92
-2	-8	92	72
-2	9	135	135
3	0	146	140
-3	0	132	133
3	-1	243	246
-3	1	99	106
-3	-1	149	151
3	-2	116	114
-3	-2	82	80
3	3	166	164
3	-3	114	109
-3	-3	218	211
-3	-4	126	123
3	-5	193	192
-3	5	120	117
-3	-5	90	77
3	-6	233	223
-3	-7	120	106
-3	-8	128	119
-3	10	142	145
4	-1	102	93
4	2	101	99
4	-2	110	109
-4	2	183	179
-4	-2	338	330
4	-3	119	105
-4	3	140	137
-4	-3	130	118
4	-4	73	47
4	-5	104	95
-4	-5	99	83
4	-6	275	238
-4	-6	92	82
4	-7	215	197
4	-10	97	85
-5	0	89	84
5	-1	97	88
-5	-1	208	211
-5	3	180	177
-5	4	308	301
5	-7	185	172
5	-8	104	107
5	-12	125	119
6	0	153	156
-6	2	127	116
-6	4	139	117
-6	-4	98	92
-6	5	191	189
7	-1	175	165
7	-2	114	90
-7	-2	131	118
-7	-3	118	97
7	-5	130	124
7	-6	121	109
7	-8	113	109
-8	-1	106	105
-8	-2	109	89
8	-7	123	111
**** H = 6 ****			
0	2	86	81
0	-2	176	174
0	-6	120	119
0	-7	226	225
-1	0	102	106
1	1	115	126
-1	2	66	79
-1	3	76	91
-1	4	85	80
1	5	138	131
1	-5	76	48
-1	-5	135	139
-1	-6	128	119
1	-7	84	74
1	-8	169	158
2	0	150	155
-2	0	122	131
2	-1	149	147
-2	1	102	102
-2	-1	53	62
-2	-2	116	125
-2	-3	111	113
2	4	133	133
-2	-4	82	80
-3	0	93	88
3	1	154	159
-3	1	93	94
-3	-1	124	132
3	-2	175	171
-3	3	119	107
-3	-4	94	86
3	-5	89	84
3	-6	94	100
-3	-7	117	100
-4	1	91	94
4	-2	149	139
-4	2	185	174
-4	-2	94	98
4	-3	125	106
-4	-3	114	103
4	-5	98	77
-4	5	96	80
-4	-5	112	86
4	-6	89	82
4	-7	130	118
4	-8	112	82
-5	3	187	187
5	-6	97	84
5	-6	4	102

TABLE IV

INTERATOMIC DISTANCES (Å) WITH STANDARD DEVIATIONS[a]

Ni(1)–Ni(2)	2.733 (7)	N(1)–H(1)	1.04 (11)
Ni(1)–S(1)	2.212 (5)	N(1)–H(2)	1.09 (11)
Ni(1)–S(2)	2.212 (4)	N(2)–H(7)	1.04 (11)
Av	2.212	N(2)–H(8)	0.96 (11)
		Av	1.03
Ni(2)–S(1)	2.154 (5)		
Ni(2)–S(2)	2.156 (3)	C(1)–H(3)	0.95 (11)
Av	2.155	C(1)–H(4)	1.07 (12)
Ni(2)–N(1)	1.902 (7)	C(2)–H(5)	1.17 (11)
Ni(2)–N(2)	1.926 (7)	C(2)–H(6)	1.02 (11)
Av	1.914	C(3)–H(9)	1.18 (10)
		C(3)–H(10)	1.02 (11)
S(1)–C(2)	1.83 (1)	C(4)–H(11)	1.27 (11)
S(2)–C(4)	1.84 (1)	C(4)–H(12)	0.96 (11)
Av	1.84	Av	1.08
N(1)–C(1)	1.49 (1)		
N(2)–C(3)	1.47 (1)	S(1)···S(2)	2.89 (1)
Av	1.48	S(1)···S(2′)	3.35 (1)
		S(1)···N(1)	2.84 (1)
C(1)–C(2)	1.50 (1)	S(2)···N(2)	2.90 (1)
C(3)–C(4)	1.51 (1)	N(1)···N(2)	2.85 (1)
Av	1.51	Cl···N(1)^{I}	3.23 (1)
		Cl···N(1)^{II}	3.24 (1)
		Cl···N(2)	3.22 (1)
		Cl···N(2)^{III}	3.73 (1)
		Cl···H(1)^{I}	2.32 (11)
		Cl···H(2)^{II}	2.20 (11)
		Cl···H(7)	2.37 (11)
		Cl···H(8)^{III}	3.34 (11)

[a] Superscripts refer to the following positions: (I) $-x, -y, -z$; (II) $1 - x, -y, -z$; (III) $x - 1, y, z$.

atoms, together with their standard deviations, are given in Tables I and II, respectively. The observed and calculated structure amplitudes are listed in Table III. The interatomic distances and bond angles with their standard deviations, calculated from the final parameters of Tables I and II by means of the Busing–Martin–Levy function and error program,[27] as modified by Johnson,[28] are shown in Tables IV and V, respectively. The root-mean-square thermal displacements along the directions of the principal axes are given for the nonhydrogen atoms in Table VI.

Discussion

General Description and Packing of the $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+}(Cl^-)_2$ Crystal Structure.—The crystal structure of tetrakis(2-aminoethanethiol)trinickel(II) chloride consists of discrete divalent $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2{}^{2+}$ cations and chloride anions. Figure 1 shows a stereoscopic view[29] of the isolated trinuclear nickel cation based on thermal parameters obtained from the final anisotropic–isotropic least-squares

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[27] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[28] C. K. Johnson, "ORFFE-II, a Modified Version of ORFFE,"[27] Oak Ridge National Laboratory, Oak Ridge, Tenn., 1966.

[29] The drawings shown in Figures 1–4 were prepared by the use of the Johnson program: C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

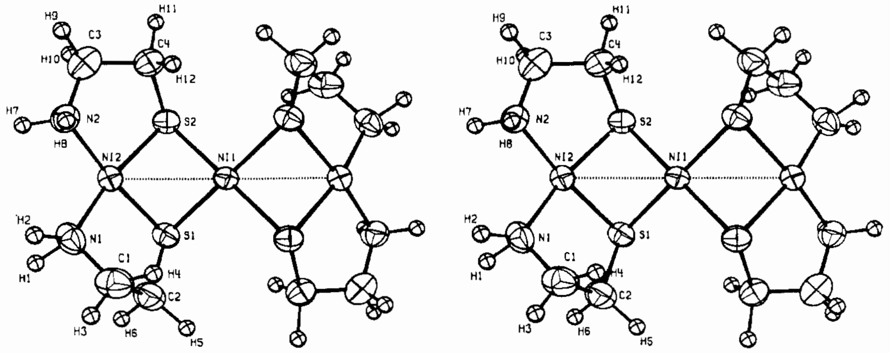

Figure 1.—Stereoscopic view of the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2^{2+}$ cation in a direction perpendicular to the linear trinickel system. All atoms are represented by 50% probability ellipsoids of thermal displacement.

TABLE V

BOND ANGLES WITH STANDARD DEVIATIONS (IN DEG)[a]

S(1)–Ni(1)–S(2)	81.4 (2)	Ni(2)–N(1)–C(1)	110.4 (6)
S(1)–Ni(1)–S(2′)	98.6 (2)	Ni(2)–N(2)–C(3)	115.0 (5)
		Av	112.7
Ni(1)–S(1)–Ni(2)	77.5 (2)	S(1)–C(2)–C(1)	110.4 (6)
Ni(1)–S(2)–Ni(2)	77.5 (2)	S(2)–C(4)–C(3)	106.9 (6)
Av	77.5	Av	108.7
S(1)–Ni(2)–S(2)	84.0 (2)	N(1)–C(1)–C(2)	108.1 (7)
S(1)–Ni(2)–N(1)	88.8 (2)	N(2)–C(3)–C(4)	110.1 (7)
S(2)–Ni(2)–N(2)	90.3 (3)	Av	109.2
Av	89.6	Cl–H(7)–N(2)	138 (8)
N(1)–Ni(2)–N(2)	96.1 (3)	Cl–H(1)^{I}–N(1)^{I}	145 (8)
S(1)–Ni(2)–N(2)	173.1 (2)	Cl–H(2)^{II}–N(1)^{II}	158 (9)
S(2)–Ni(2)–N(1)	168.7 (2)		
Av	170.9		
Ni(1)–S(1)–C(2)	114.0 (3)		
Ni(1)–S(2)–C(4)	112.7 (3)		
Av	113.4		
Ni(2)–S(1)–C(2)	98.5 (3)		
Ni(2)–S(2)–C(4)	96.2 (3)		
Av	97.4		

[a] Superscripts refer to the following positions: (I) $-x, -y, -z$; (II) $1 - x, -y, -z$.

TABLE VI

ROOT-MEAN-SQUARE THERMAL DISPLACEMENTS ALONG THE DIRECTION OF THE PRINCIPAL AXES (IN Å)

Atom	Axis 1	Axis 2	Axis 3
Ni(1)	0.172 (2)	0.189 (2)	0.196 (2)
Ni(2)	0.184 (2)	0.191 (1)	0.195 (2)
S(1)	0.190 (3)	0.194 (2)	0.222 (3)
S(2)	0.181 (3)	0.198 (2)	0.216 (3)
Cl	0.224 (2)	0.233 (3)	0.258 (3)
N(1)	0.186 (10)	0.205 (8)	0.272 (10)
N(2)	0.186 (9)	0.212 (9)	0.258 (8)
C(1)	0.215 (12)	0.220 (11)	0.290 (12)
C(2)	0.201 (12)	0.234 (10)	0.267 (11)
C(3)	0.217 (12)	0.247 (10)	0.277 (11)
C(4)	0.189 (9)	0.224 (11)	0.230 (11)

refinement. The crystallographically independent chloride ion is not in one of the octahedral-like positions about a nickel atom but is well separated by a distance of 3.61 Å from the nearest nickel atom Ni(2) with an Ni(1)···Ni(2)···Cl angle of 154°. This X-ray diffraction analysis thereby establishes the existence of a new kind of trinuclear metal complex whose overall geometry conforms with that proposed by Jicha and Busch.[7]

Figure 2 shows the [100] projection of the $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$ unit cell. In this crystal structure each chloride ion makes its closest contacts with three amine nitrogen atoms of the surrounding three symmetry-related cations, with $N\cdots Cl^-$ distances of 3.22 (1), 3.23 (1), and 3.24 (1) Å. These relatively short $NH\cdots Cl^-$ distances suggest that the crystal is partially stabilized by hydrogen bonding, in that they are compatible with those of 3.15–3.51 Å listed for methylglyoxal bisguanylhydrazone dihydrochloride monohydrate (MBDM);[30] with those of 3.26, 3.28, and 3.39 Å given for bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride monohydrate;[31] and with those of 3.22, 3.25, 3.26, and 3.36 Å found for bis-

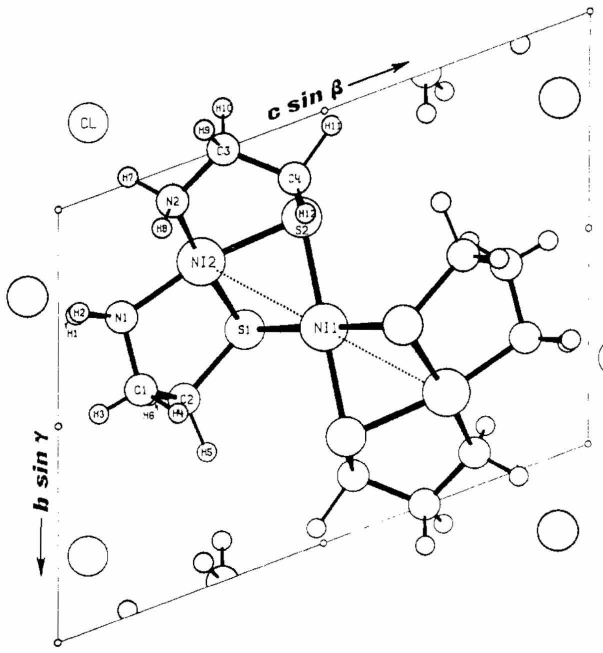

Figure 2.—[100] projection of the centrosymmetric triclinic unit cell containing one ionic $[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]^{2+}(Cl^-)_2$ formula species.

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[30] (a) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968, p 184; (b) W. A. Hamilton and S. J. La Placa, *Acta Crystallogr.*, **B24**, 1147 (1968).

[31] E. O. Schlemper, *Inorg. Chem.*, **7**, 1130 (1968).

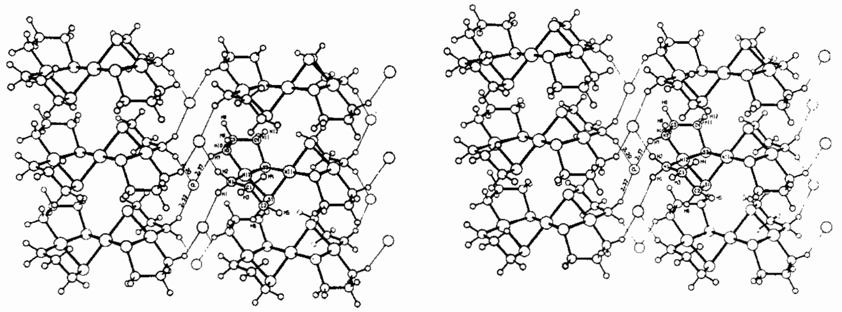

Figure 3.—Stereoscopic view of the packing with indicated $NH\cdots Cl^-$ interactions. A trinuclear nickel cation is surrounded by six crystallographically related chloride ions, each of which is hydrogen bonded to three amine nitrogen atoms.

(ethylenediamine)palladium(II) chloride, $Pd(en)_2Cl_2$.[32] These observed $NH\cdots Cl^-$ distances also fall within the range of 2.91–3.41 Å tabulated for $N^+\ldots Cl^-$ distances.[33] The N(1) atom, in turn, is hydrogen bonded to its two nearest Cl^- anions. The three $Cl^-\cdots H$ distances of 2.20 (11), 2.32 (11), and 2.37 (11) Å compare favorably with those of 2.17–2.82 Å tabulated for MBDM[30a] and with 2.24, 2.40, 2.43, and 2.44 Å given for $Pd(en)_2Cl_2$.[32] The three $N\text{-}H\cdots Cl^-$ angles involved in the hydrogen bonding deviate markedly from linearity, being 138 (8), 145 (8), and 158 (9)°. This network of hydrogen bonding results in the formation of infinite sheets parallel to both the $[0\bar{1}1]$ and [100] directions of the unit cells. Figure 3, a stereoscopic drawing of this network, shows $NH\cdots Cl^-$ interactions about a given cation as well as those involving a given chloride ion.

Stereochemistry of a $M'\{MX_2Y_2\}_2{}^n$ System.—The overall geometry of the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2{}^{2+}$ cation may be regarded as the first structurally proven representative member of a basic trinuclear metal complex of general formula $M'\{MX_2Y_2\}_2{}^n$ where X and Y each represent a metal-coordinated atom of a donor ligand (*i.e.*, either mono-, bi-, or polydentate). The two identical MX_2Y_2 entities of *cis* configuration are chelated to the central metal atom M′ by four M′–Y bonds such that M′ is surrounded by four bridging Y ligands. The disposition of the eight X and Y atomic ligands about the M_3 fragment (assumed in this general representation to be linear) can be visualized as a *trans* fusion of a central $M'Y_4$ unit with two MX_2Y_2 units along the Y–Y lines. The three metal atoms in such an atomic arrangement may also be interconnected by metal–metal interactions (*vide infra*).

A C_{2h}-2/m model can occur when the fusion of *planar* MX_2Y_2 and $M'Y_4$ units gives rise to a nonplanar fragment. This model is exemplified by the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2{}^{2+}$ cation where X = N, Y = S, and M′ = M = Ni(II) and where one NiS_4 and two NiN_2S_2 units are each approximately planar. The particular trigonal-pyramidal conformation of each of the four nickel-coordinated sulfur atoms, which is due to the steric requirements of the chelating $NH_2CH_2CH_2S$ ligands, necessitates that the intersection of a planar NiN_2S_2 entity with the planar NiS_4 one along the sulfur–sulfur line be at a torsional angle[34] of considerably less than 180°. In agreement with the postulation of Jicha and Busch,[7] the observed bending of the two pairs of adjacent planes along the common sulfur–sulfur lines yields a chair conformation for which the torsional angle[34] between each NiN_2S_2 unit and the NiS_4 unit is found to be 109°. The experimental conformity of the nickel–sulfur–nitrogen fragment, $Ni\{NiN_2S_2\}_2$, to C_{2h} symmetry is readily seen in Table VIIc which shows variations of less than 0.01 Å in the

TABLE VII

EQUATIONS OF BEST MOLECULAR PLANES AND PERPENDICULAR DISTANCES (Å) OF ATOMS FROM THESE PLANES[a]

(a) Plane through S(1), S(2), S(1′), and S(2′)

$$0.704X + 0.090Y - 0.705Z + 2.099 = 0$$

Ni(2)	1.47	C(1)	2.54	C(4)	1.18
N(1)	2.71	C(2)	1.11		
N(2)	2.71	C(3)	2.17		

(b) Plane through S(1), S(2), N(1), and N(2)

$$-0.723X - 0.603Y - 0.337Z + 2.896 = 0$$

S(1)	0.006	Ni(1)	−1.57	C(3)	0.12
S(2)	−0.005	Ni(2)	0.12	C(4)	−0.63
N(1)	−0.072	C(1)	−1.03		
N(2)	0.078	C(2)	−0.58		

(c) Plane through Ni(1), Ni(2), Midpoint of S(1)–S(2), and Midpoint of N(1)–N(2)

$$-0.477X + 0.790Y - 0.386Z + 1.208 = 0$$

Ni(1)	−0.000	S(1)	1.45	C(1)	2.45
Ni(2)	−0.000	S(2)	−1.45	C(3)	−2.80
MP S(1)–S(2)	0.000	N(1)	1.43	C(2)	2.90
MP N(1)–M(2)	0.001	N(2)	−1.43	C(4)	−2.85

[a] The equation of each weighted least-squares plane is expressed in orthogonal coordinates (X, Y, Z) which are related to the triclinic cell coordinates (x, y, z) by the transformation: $X = x \sin \gamma + z \cos \varphi$, $Y = y + z \cos \alpha + x \cos \gamma$, and $Z = z \cos \rho$ where $\cos \varphi = (\cos \beta - \cos \gamma \cos \alpha)/\sin \gamma$ and $\cos \rho = (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}/\sin \gamma$. In this transformation X lies in the xy plane, Y coincides with y, and Z is perpendicular to the xy plane. The weighting factor, w_k, given to each atom "k" forming the plane was $w_k = [a\sigma(x_k)b\sigma(y_k)c\sigma(z_k)]^{-2/3}$ where $\sigma(x_k)$, $\sigma(y_k)$, and $\sigma(z_k)$ are the standard deviations in fractional coordinates of the atomic coordinates x_k, y_k, and z_k, respectively.[35]

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[32] J. R. Wiesner and E. C. Lingafelter, *Inorg. Chem.*, **5**, 1770 (1966).

[33] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p 290.

[34] The torsional angle is here defined as the angle directly between the two planes; in previous papers this angle has also been called a dihedral angle. The usage here of dihedral angle is to refer to the angle between the normals of two planes.

[35] D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, Madison, Wis., 1962.

perpendicular distances of the chemically equivalent atoms related to each other by the horizontal mirror plane[35] passing through the three nickel atoms and the midpoints of the sulfur atoms, S(1) and S(2), and the nitrogen atoms, N(1) and N(2). The twofold axis perpendicular to this mirror plane passes through the central nickel atom. Inclusion of the methylene groups in the Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation lowers the symmetry from C_{2h} to the crystallographically observed C_i-$\bar{1}$.

Depending upon the electronic and steric requirements of both the metal and ligand atoms, several other idealized structural models of different symmetry should also be considered for the M'$\{MX_2Y_2\}_2{}^{n}$-type complex. With nonchelating groups the possibility exists that the amalgamation of the *planar* MX_2Y_2 and *planar* M'Y_4 units will result in a D_{2h}-2/m2/m2/m model in which the M', X, and Y atoms are all essentially coplanar. On the other hand, the fusion of two *planar* MX_2Y_2 groups with a *tetrahedral-like* M'Y_4 central unit will form a C_1-1 model if (due to steric effects of chelating XY ligands such as 2-aminoethanethiol) there is a folding along the two Y–Y lines; both the Cu$\{$Ni($NH_2CH_2CH_2S)_2\}_2{}^{+}$ and Cd$\{$Ni($NH_2CH_2CH_2S)_2\}_2{}^{2+}$ cations[7] presumably conform to this model containing no symmetry. If there is no Y–Y folding (because of the absence of any ligand steric constraints), this latter model may attain tetragonal D_{2h}-$\bar{4}$2m symmetry.

The Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ Cation.—The important distances and angles for the nonhydrogen part of the cation are given in Figure 4. The central nickel atom Ni(1) and the four attached sulfur atoms are required by the crystallographic center of symmetry, located at Ni(1), to be exactly planar. The deviation of the four coordinated sulfur ligands of Ni(1) from square planarity is revealed from the S(1)–Ni(1)–S(2) angle of 81.4 (2)°. Each of the two outside nickel atoms, Ni(2) and Ni(2'), is perpendicularly displaced from its mean plane[35] of two sulfur and two nitrogen atoms (Table VIIb) by 0.12 Å in the direction opposite to the side of the central nickel atom Ni(1).

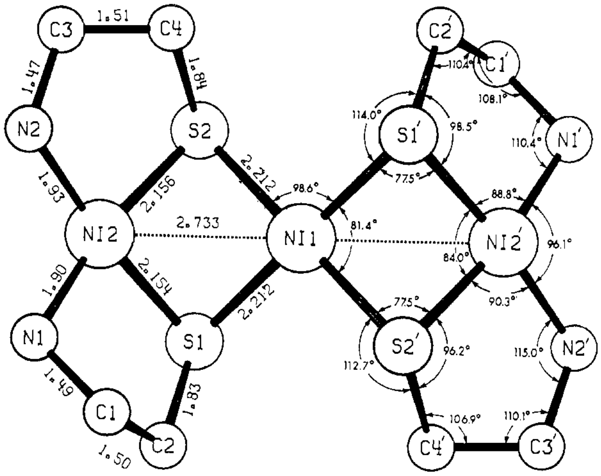

Figure 4.—Principal bond lengths and angles for Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation that possesses a crystallographic center of symmetry.

It is particularly informative to relate the structural features of the Ni$\{NiN_2S_2\}_2$ fragment of the Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation with those of the corresponding [Ni(S_2P)]$_2$ moiety of the dinuclear mercaptophosphinenickel(II) complex[36] of formula [Ni($SCH_2CH_2)_2PR]_2$ (where R represents CH_2CH_2SH). The nonplanar [Ni(S_2P)]$_2$ fragment of this latter complex can be viewed as being formed by the fusion of the two planar NiS_3P units along an S–S edge with the two phosphorus atoms *trans* to each other such that the resulting symmetry of this fragment (and the entire molecule) is C_2-2. As with the chair conformation of the Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation, the noncoplanarity of these two intersecting planes can be attributed to the steric chelation requirements of the two tridentate ($SCH_2CH_2)_2PR$ ligands. This folding of the dinuclear nickel molecule along the S–S line occurs to such an extent that the Ni(II)–Ni(II) distance of only 2.647 Å compares favorably with the two crystallographically identical Ni(II)–Ni(II) distances of 2.733 (7) Å in the Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation. The resulting similarity between the conformation of the dinuclear nickel(II) fragment and that of the trinuclear nickel(II) fragment (which from a coordination standpoint may be simply regarded as an extension of the dinuclear nickel(II) system) is also accented by the unusually acute Ni–S–Ni bridging angles of 77.5 (2)° (average) in the trinuclear nickel fragment and 73.2° in the dinuclear nickel fragment, because of the bending of both molecules along the S–S lines. It is noteworthy that Schwarzenbach[36] also reported the preparation of the tetrakis(β-mercaptophosphine)-trinickel(II) cation of formula Ni$\{$Ni($PR_2CH_2CH_2S)_2\}_2^{2+}$ (R = C_2H_5), which no doubt must be stereochemically analogous to the electronically equivalent Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation.

The Ni–S bond lengths of the Ni$\{NiN_2S_2\}_2$ fragment of the Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation closely adhere to C_{2h}-2/m symmetry. The average bonding distance of 2.212 (3) Å from the sulfur atoms to the central nickel(II) atom, Ni(1), is distinguishably longer than the average bonding distance of 2.155 (3) Å from the sulfur atoms to the terminal nickel(II) atoms, Ni(2) and Ni(2'). A comparison of the average bond lengths in the Ni$\{$Ni($NH_2CH_2CH_2S)_2\}_2^{2+}$ cation with corresponding relevant bond lengths found in other metal complexes is given in Table VIII. It is seen that the various values observed in the trinuclear nickel(II) cation are close to those found for these other complexes.

The carbon atoms of the two independent 2-aminoethanethiol ligands coordinated to the nickel(II) atoms possess two distinct *gauche* conformations as found in other 2-aminoethanethiol and ethylenediamine chelating structures.[32,37,38] That the orientations of the

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TABLE VIII

COMPARISON OF AVERAGE INTERATOMIC DISTANCES (Å) WITH THOSE OF SQUARE-PLANAR COMPLEXES[a,b]

Compound	Ni···Ni	Ni–S	Ni–N(amine)	C–N(amine)	C–C	S–C	Ref
$[Ni\{Ni(NH_2CH_2CH_2S)_2\}_2]Cl_2$	2.733 (7)	2.212 (3), 2.155 (3)	1.91 (1)	1.48 (1)	1.51 (1)	1.84 (1)	*c*
$Ni[NH_2NC(NH_2)S]_2$		2.155 (3)	1.91 (1)				*d*
α-$Ni(CH_5N_3S)_2SO_4 \cdot 3H_2O$		2.16 (1)	1.90 (2)				*e*
$Ni(C_{14}H_{16}N_2)_2(Cl_2CHCOO)_2 \cdot {}^2/_3C_2H_5OH \cdot {}^4/_3H_2O$ (yellow form)			1.89 (3)				*f*
$[Ni(SC_2H_5)_2]_6$	2.92 (1)	2.20 (2)					*g*
$Ni_3(CH_3COCH_2COCH_3)_6$	2.889 (18)						*h*
$[(CH_3)_4N]_2Ni[S_2C_2(CN)_2]_2$		2.165 (4)					*i*
$Ni(CH_3CNCH_2CH_2S)_2$		2.157 (8)			1.44 (5)	1.82 (3)	*j*
$Ni[(C_2H_5)_2NCS_2]_2$		2.201 (1)					*k*
$[Ni(SCH_2CH_2)_2P(CH_2CH_2SH)]_2$	2.647[l]	2.220, 2.158			1.54	1.85	*m*
$Pd[NH_2(CH_2)_2NH_2]_2Cl_2$				1.48 (1)	1.52 (1)		*n*
$PCH_3(C_6H_5)_3Ni[S_2C_2(CN)_2]_2$		2.146 (1)					*o*
$Ni(C_2H_4ONS)_2$		2.15 (1)					*p*
$Ni[(C_6H_5)_2C_2S_2]_2$		2.101 (2)					*q*
$Ni(NH_2CS_2)_2$		2.215 (6)					*r*
$C_4H_{10}NiO_2S_2$		2.15 (3)					*s*
$NiC_7H_7ON_5S_4$		2.155					*t*
$Ni[SC_2H_4N(CH_3)_2]_2$		2.198 (3)			1.51 (2)	1.82 (2)	*u*
$C_{10}H_{23}N_4O_2NiCl \cdot H_2O$			1.91 (1)	1.52 (1)	1.54 (1)		*v*
$[(C_6H_5)_4As]_2[Ni(S_2CNCN)_2]$		2.189 (5)					*w*
$Ni[S_2P(C_6H_5)_2]_2$		2.238 (4)					*x*

[a] Each C, N, and S atom possesses a tetrahedral coordination. [b] In case the average value and/or its standard deviation are not given by the individual author(s), the average value was calculated as the arithmetic mean, and the standard deviation, σ, was estimated as $\sigma_{av}/\sqrt{n}$ where σ_{av} refers to the average of the standard deviations and n stands for the number of values averaged. [c] This paper. [d] L. Cavalca, M. Nardelli, and G. Fava, *Acta Crystallogr.*, **15,** 1139 (1962). [e] G. Grønbaek and S. E. Rasmussen, *Acta Chem. Scand.*, **16,** 2325 (1962). [f] S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3,** 468 (1964). [g] P. Woodward, L. F. Dahl, E. W. Abel, and C. Crosse, *J. Amer. Chem. Soc.*, **87,** 5251 (1965). [h] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4,** 456 (1965). [i] R. Eisenberg and J. A. Ibers, *ibid.*, **4,** 605 (1965). [j] Q. Fernando and P. J. Wheatley, *ibid.*, **4,** 1726 (1965). [k] M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19,** 619 (1965). [l] Value calculated from other related molecular parameters given. [m] Reference 36. [n] Reference 32. [o] C. J. Fritchie, Jr., *Acta Crystallogr.*, **20,** 107 (1966). [p] T. Sato, K. Nagata, M. Shiro, and H. Koyama, *Chem. Commun.*, 192 (1966). [q] D. Sartain and M. R. Truter, *ibid.*, 382 (1966). [r] L. Capacchi, M. Nardelli, and A. Villa, *ibid.*, 441 (1966). [s] R. O. Gould and R. M. Taylor, *Chem. Ind.* (*London*), 378 (1966). [t] J. Weiss and U. Thewalt, *Z. Anorg. Allg. Chem.*, **343,** 274 (1966). [u] Reference 37. [v] E. O. Schlemper, *Inorg. Chem.*, **7,** 1130 (1968). [w] F. A. Cotton and C. B. Harris, *ibid.*, **7,** 2140 (1968). [x] P. Porta, A. Sgamellotti, and N. Vinciguerra, *ibid.*, **7,** 2625 (1968).

dimethylene fragments in the two independent NH_2-CH_2CH_2S ligands are different from each other is apparent from the molecular view in Figure 4, which shows distinct variations in the corresponding ring angles. Examination of the locations of the corresponding methylene carbon atoms in the two chelating ligands on the opposite sides of the previously mentioned pseudomirror plane that passes through the $Ni\{NiN_2S_2\}_2$ fragment (Table VIIc) shows that C(2) and C(4) are approximately equidistant (2.90 and 2.85 Å, respectively) from this mirror plane, while C(1) and C(3) are located at considerably different perpendicular distances (2.45 and 2.80 Å, respectively). This asymmetric arrangement of C(1) and C(3) with respect to each other is also reflected in these two atoms being located 1.03 Å above and 0.12 Å below the mean N_2S_2 plane (Table VIIb), in contrast to C(2) and C(4) being at similar perpendicular distances of 0.58 and 0.63 Å from this plane.

The four independent N–H distances range from 0.96 to 1.09 Å (esd 0.11 Å), while the eight independent C–H distances vary from 0.96 to 1.27 Å (esd 0.11 Å). These variances are not statistically significant from the average values of 1.03 (6) Å for the N–H bond length and 1.08 (4) Å for the C–H bond length.

It is known that the inclusion of hydrogen atoms in the refinement of a structure can markedly improve the individual atomic parameters of nonhydrogen atoms.[39] The sensitivity of molecular parameters to the inclusion of hydrogen atoms in this structure is made apparent by the more reasonable agreement of the N(1)–C(1) distance of 1.49 (1) Å with the N(2)–C(3) distance of 1.47 (1) Å compared to the corresponding values of 1.54 (1) and 1.48 (1) Å, respectively, obtained when no hydrogen atoms were included in the anisotropic thermal least-squares refinement of the structure.

The Ni(II)–Ni(II) Interactions in the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2^{2+}$ Cation and in $[Ni(SCH_2CH_2S)_2P(CH_2CH_2SH)]_2$.—Although it is concluded here that the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2^{2+}$ cation and the neutral $[Ni(SCH_2CH_2)_2P(CH_2CH_2SH)]_2$ molecule adopt their molecular architectures primarily as a consequence of the steric requirements of the chelating ligands, the short Ni(II)–Ni(II) distances of 2.733 (7) and 2.647 Å, respectively, imply the possibility that a weak net bonding effect may result from the Ni(II)–Ni(II) interactions. The following qualitative MO symmetry arguments applied to both of these complexes clearly

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(39) This effect was cited in the refinement of dichlorobis(2-amino-2-methyl-3-butanone oximato)cobalt(III): E. O. Schlemper, S. J. La Placa, and W. C. Hamilton, Abstracts of Papers, Winter Meeting of the American Crystallographic Association, Seattle, Wash., March 23–28, 1969, p 29.

indicate the conditions necessary for any weak positive interaction to occur. Each nickel(II) atom of d^8 electronic configuration has available a filled $3d_{z^2}$ atomic orbital and an empty $4p_z$ one for possible metal–metal interaction by overlap with corresponding orbitals on the neighboring nickel(II) atoms.[40] (The other Ni(II) valence orbitals are assumed to retain their localized character and not to play dominant roles concerning the *net* metal–metal interactions; for simplicity it is presumed that the 4s nickel(II) orbital is completely utilized in σ bonding to the four planar ligand atoms of each nickel(II) such that a "pure" $3d_{z^2}$ orbital rather than a hybrid $3d_{z^2}$–4s one of unknown weighting coefficients is involved in the Ni(II)–Ni(II) interactions. These arbitrary boundary conditions do not significantly affect the conclusions reached from these MO rationalizations.) For the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2^{2+}$ cation (Figure 5) the d_{z^2} basis functions of the three nickel(II) atoms transform according to the irreducible representations of the C_{2h}-2/m site symmetry of the $Ni\{NiN_2S_2\}_2$ fragment to give (with the neglect of nonadjacent nickel–nickel interactions) a three-center bonding $\mathbf{a}_g$ combination $a(d_{z_2^2} + d_{z_{2'}^2}) + bd_{z_1^2}$ (where the orbital subscript 1 refers to the central nickel atom, and 2 and 2′ refer to the symmetry-related terminal nickel atoms), a nonbonding $\mathbf{b}_u$ combination $c(d_{z_2^2} - d_{z_{2'}^2})$, and an antibonding $\mathbf{a}_g$ combination $b(d_{z_2^2} + d_{z_{2'}^2}) - ad_{z_1^2}$; similarly, the three $4p_z$ orbitals will form a three-center bonding $\mathbf{b}_u$ combination $e(p_{z_2} - p_{z_{2'}}) + fp_{z_1}$, a nonbonding $\mathbf{a}_g$ combination $g(p_{z_2} + p_{z_{2'}})$, and an antibonding $\mathbf{b}_u$ combination $f(p_{z_2} - p_{z_{2'}}) - ep_{z_1}$. To the extent that any mixing of the $4p_z$ orbital combinations with the $3d_{z^2}$ orbital combinations of the same representation is neglected, the three nondegenerate metal symmetry combinations (SO's) of essentially "pure" d_{z^2} character will each be fully occupied, which will lead to a net energy destabilization of the trinuclear nickel(II) cation because of Ni(II)–Ni(II) interactions. However, the lowering of the energies of these three SO's by contributions of p_z character, mainly to the antibonding $\mathbf{a}_g$ d_{z^2} SO from the higher energy virtual $\mathbf{a}_g$ p_z SO (through configurational interaction) and to the nonbonding $\mathbf{b}_u$ d_{z^2} SO from primarily the empty bonding $\mathbf{b}_u$ p_z SO, may be sufficient to result in a net bonding stabilization. In the case of the $[Ni(SCH_2CH_2)_2P(CH_2CH_2SH)]_2$ molecule, under C_2-2 symmetry the interactions of the d_{z^2} orbitals of the two nickel(II) atoms give rise to bonding **a** and antibonding **b** SO's; the bonding and antibonding SO's formed from the two empty $4p_z$ orbitals also belong to the **a** and **b** representations, respectively. Again, inclusion of $4p_z$ orbital character into the filled bonding and antibonding $3d_{z^2}$ combinations by mixing of the SO's of the same representation is necessary to produce any net molecular stability from the Ni(II)–Ni(II) interaction.

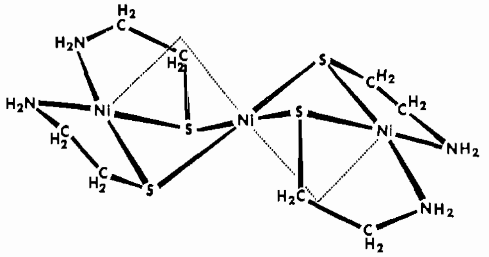

Figure 5.—General configuration of the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2^{2+}$ cation with the indicated nickel(II)–nickel(II) interactions of the trinickel system.

These same kinds of qualitative MO representations were first applied by Rundle[41] and later by Miller[42] to a variety of Ni(II), Pd(II), Pt(II), and other d^8 metal atom four-coordinated planar complexes (such as bis(dimethylglyoximato)nickel(II)[43]) which crystallize to give one-dimensional metal chains normal to the molecular ligand planes. Rundle[41] and Miller[42] both suggested that the valence d_{z^2} and p_z orbitals in these chains of metal atoms overlap to form delocalized band-type orbitals. Rundle[41] argued that the Ni(II)–Ni(II) interactions in bis(dimethylglyoximato)nickel(II) were of sufficient positive strength to account for the compound's relative insolubility and its unusual optical properties; however, Miller[42] and others[44–46] concluded that the overall ground-state metal–metal interaction in this complex is probably antibonding such that the structure is formed in spite of the metal–metal interaction. Invariant to the extent of metal–metal interaction in the ground electronic state of bis(dimethylglyoximato)nickel(II) and other d^8 metal complexes, recent experimental studies[47–50] have shown some of these complexes to exhibit anisotropic electron conductivity along the metal–metal chain; the semiconductor properties of such complexes no doubt involve electron excitation to unoccupied band-type orbitals. Furthermore, from systematic studies Krogmann and coworkers[51] found that bonding in the metal–metal chains of a number of platinum(II) complexes can be strengthened by partial oxidation with observed reduction in Pt–Pt bond distances.

The fact that the Ni(II)–Ni(II) distances in both the $Ni\{Ni(NH_2CH_2CH_2S)_2\}_2^{2+}$ cation and the $[Ni(SCH_2CH_2)_2P(CH_2CH_2SH)]_2$ molecule are 0.5 Å shorter than

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(40) The orbital combinations given for both the dinuclear and trinuclear nickel complexes are based on a localized right-handed coordinate scheme for each nickel atom with the *z* axis chosen perpendicular to the plane of the four attached ligand atoms. For the dinickel complex the *z* axis of each of the equivalent nickel atoms is directed toward the other half of the molecule; in the trinickel complex the *z* axis of each terminal nickel atom is directed toward the central nickel atom.

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the Ni(II)–Ni(II) distance of 3.245 Å in bis(dimethylglyoximato)nickel(II)[43] supports the premise that if a *weak* positive kind of metal–metal interaction is operative in bis(dimethylglyoximato)nickel(II), then it is probably operative in the trinuclear nickel(II) cation and dinuclear nickel(II) molecule as well, especially if low-lying excited electronic states are assumed to mix with the ground state.

To the extent that these nickel(II)–nickel(II) interactions have any important influence on the chemistry of the trinuclear nickel(II) cation, it may be expected that the electron density of the terminal Ni(II) atoms along the *z* direction approximately normal to the four-coordinated NiS_2N_2 plane would be localized on the exterior side opposite from the center Ni(1) atom. Any significant localization of negative charge in the external *z* direction should make this complex more susceptible to coordination with a Lewis acid.

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Raman and Infrared Frequencies, Force Constants, and Bond Polarizability Derivatives for Trimethylplatinum Hydroxide, Chloride, and Iodide[1a]

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Raman and infrared spectra have been obtained for the tetrameric molecules $[(CH_3)_3PtX]_4$ where X = OH, Cl, and I. For the hydroxide and chloride, single-crystal Raman polarizations provide unambiguous determination of the symmetry species of the observed frequencies. Assignments to internal coordinates were made by intercomparisons of the spectra and comparisons with related molecules. Of particular interest is the observation in each case of a set of three strong low-frequency bands in the Raman spectrum, with frequency ratios close to those predicted for a tetrahedron of like atoms bound to one another in the "simple cluster" approximation. Normal-coordinate analyses were carried out using force fields containing a force constant for metal–metal interaction. Absolute Raman intensities were measured for the totally symmetric modes and used to calculate bond polarizability derivatives and estimate bond orders. The results indicate that bonds between the platinum atoms and the bridging X atoms are weak and highly ionic. The Raman intensities provide evidence for weak interaction between platinum atoms, which decreases with increasing internuclear distance along the series X = OH, Cl, and I. The force constants for Pt–Pt stretching decrease in the same order but are much larger than expected in relation to the weakness of the Pt–Pt interaction. The bonding pattern is similar to that found previously for the oxygen-bridged complexes $Bi_6(OH)_{12}{}^{6+}$, $Pb_4(OH)_4{}^{4+}$, and $Tl_4(OC_2H_5)_4$.

Introduction

As part of a continuing study[2–8] of the vibrational spectra of bridged polynuclear metal complexes we have investigated the Raman and infrared spectra of the compounds $[(CH_3)_3PtX]_4$, where X = OH, Cl, I. Of particular interest was the possibility of observing and more completely characterizing the type of strong low-frequency lines found in the Raman spectra of $Bi_6(OH)_{12}{}^{6+}$,[2] $Pb_4(OH)_4{}^{4+}$,[3] and $Tl_4(OR)_4$.[4]

The crystal structure of trimethylplatinum hydroxide, $(CH_3)_3PtOH$, has recently been completely determined[9,10] and shows the presence of discrete tetrameric units, with the platinum atoms and hydroxyl oxygens arranged in interpenetrating tetrahedra. Three methyl groups are attached to each Pt atom in such a way as to preserve the T_d symmetry of the molecule. This structure is shown in Figure 1. An analogous structure had been found previously for trimethylplatinum chloride,[11] although the carbon atoms were not located. A partial structure determination for the iodide[12] also shows the presence of this type of tetrameric unit, but indicates a slight reduction of the T_d symmetry and a different

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[1] (a) This investigation was supported by Public Health Service Grant GM-13498, from the National Institute of General Medical Sciences, and by National Science Foundation Grant GP-10122. (b) NASA Trainee, 1966–1969. (c) NASA Trainee, 1964–1966.

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