Brown, I. D. (1981). *Struct. Bonding (Berlin)*, **2**, 1–30.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, pp. 149–150. Birmingham: Kynoch Press.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72 ff. Birmingham: Kynoch Press.

Faggiani, R., Lippert, B., Lock, C. J. L. & Rosenberg, B. (1977a). *J. Am. Chem. Soc.* **99**, 777–781.

Faggiani, R., Lippert, B., Lock, C. J. L. & Rosenberg, B. (1977b). *Inorg. Chem.* **16**, 1192–1196.

Faggiani, R., Lippert, B., Lock, C. J. L. & Rosenberg, B. (1978). *Inorg. Chem.* **17**, 1941–1945.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Hughes, R. P., Krishnamachari, N., Lock, C. J. L., Powell, J. & Turner, G. (1977). *Inorg. Chem.* **16**, 314–319.

Johnson, C. K. (1976). *ORTEP*-II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Lippert, B., Lock, C. J. L., Rosenberg, B. & Zvagulis, M. (1977). *Inorg. Chem.* **16**, 1525–1529.

Lippert, B., Lock, C. J. L., Rosenberg, B. & Zvagulis, M. (1978). *Inorg. Chem.* **17**, 2971–2975.

Melanson, R., Hubert, J. & Rochon, F. D. (1975). *Can. J. Chem.* **53**, 1139–1143.

Melanson, R. & Rochon, F. D. (1978). *Acta Cryst.* B**34**, 3594–3598.

Melanson, R. & Rochon, F. D. (1979). *Can. J. Chem.* **57**, 57–61.

Melanson, R., Rochon, F. D. & Hubert, J. (1979). *Acta Cryst.* B**35**, 736–738.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

Pippy, M. E. & Ahmed, F. R. (1978). *Mean Plane and Torsion Angles*, Report NRC-22, National Research Council of Canada, Ottawa.

Schmidtke, H.-H. & Garthoff, D. (1968). *Inorg. Chim. Acta*, **2**, 357–362.

Sheldrick, G. M. (1976). *SHELX.* Program for crystal structure determination and refinement. Univ. of Cambridge, England.

Stewart, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446, Computer Science Center, Univ. of Maryland, College Park, Maryland.

Watt, G. W. & Cude, W. A. (1968). *Inorg. Chem.* **7**, 335–338.

Anomalous Scattering by Praseodymium, Samarium and Gadolinium and Structures of their Ethylenediaminetetraacetate (edta) Salts

By Lieselotte K. Templeton, David H. Templeton, Allan Zalkin and Helena W. Ruben

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, USA

Abstract

$Na[Pr(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$ ($M_r = 596.24$) is orthorhombic, space group $Fdd2$, with $a = 19.589$ (3), $b = 35.763$ (5), $c = 12.121$ (2) Å, $U = 8491.5$ Å^3, $Z = 16$, $D_x = 1.865$ Mg m^{-3}, μ(Mo $K\alpha$) = 2.38 mm^{-1}. For the isomorphous Sm salt ($M_r = 605.68$): $a = 19.503$ (11), $b = 35.596$ (17), $c = 12.119$ (5) Å, $U = 8413.4$ Å^3, $Z = 16$, $D_x = 1.913$ Mg m^{-3}, μ(Mo $K\alpha$) = 2.90 mm^{-1}. For the isomorphous Gd salt ($M_r = 612.58$): $a = 19.409$ (3), $b = 35.477$ (4), $c = 12.119$ (1) Å, $U = 8344.8$ Å^3, $Z = 16$, $D_x = 1.950$ Mg m^{-3}, μ(Mo $K\alpha$) = 3.29 mm^{-1}. The structures were refined to R values of 0.037, 0.030, and 0.024 respectively for 3449, 3368 and 3386 diffraction data measured with Mo $K\alpha$ X-rays. Anomalous-scattering terms f'' derived for this wavelength are 2.87 (11), 3.64 (10), and 3.91 (9) e atom^{-1} respectively for Pr, Sm and Gd, in good agreement with theoretical values.

Introduction

To measure anomalous scattering of X-rays by rare-earth elements in experiments with synchrotron radiation (Templeton, Templeton & Phizackerley, 1980; Templeton, Templeton, Phizackerley & Hodgson, 1982) we needed the crystal structure parameters for sodium (ethylenediaminetetraacetato)praseodymate(III) octahydrate and the isomorphous Sm and Gd salts. In this paper we report determinations of these three structures using Mo $K\alpha$ radiation. Values of

the anomalous-scattering terms for this wavelength, derived from these diffraction data, are also reported.

These salts and several others crystallize according to the orthorhombic space group $Fdd2$ (Hoard, Lee & Lind, 1965). This Sm salt was used by Koetzle & Hamilton (1975) to measure anomalous neutron scattering, and Koetzle (1978) kindly gave us the parameters determined in that work. We repeated the determination for Sm using X-rays so that the synchrotron experiments could be analyzed with atomic form factors identical (apart from anomalous-scattering terms) with those used in the structure determination. Nassimbeni, Wright, van Niekerk & McCallum (1979) reported the structure of the Dy salt in this space group with parameters similar to those found for these other salts. We have adopted their scheme of atomic identification and choice of asymmetric unit to simplify comparison. However, all the crystals that we have tested of the Dy compound, and also the Ho one, are monoclinic, but with a structure very nearly the same as the orthorhombic one. A refinement of this monoclinic structure will be reported elsewhere.

Experimental

The compounds were made from oxides of Pr ('99·8%'), Sm ('99·9%') and Gd ('99·98%') from Research Chemical Corporation and $Na_2H_2(edta).2H_2O$ from Aldrich Chemical Company. The oxide was dissolved in HCl and mixed with a hot solution of the edta salt. The pH was adjusted to about 5 with sodium hydroxide. Crystals were grown by slow cooling or slow evaporation. Larger crystals were grown by slow evaporation after dissolving the first crops in hot water.

Crystals were mounted on glass fibers with epoxy glue. Data were measured with a Picker FACS-I diffractometer for Pr and Sm and with an Enraf–Nonius CAD-4 instrument for Gd, all using Mo $K\alpha$ X-rays (graphite monochromator, $\lambda = 0.70930$ Å for

$K\alpha_1$). Crystal data and other details are listed in the *Abstract* and in Table 1.

Faces of the types $\{111\}$, $\{11\bar{1}\}$, $\{131\}$ and $\{13\bar{1}\}$ occur most frequently. Many crystals exhibit only two or three of these forms in accord with the $mm2$ symmetry, but which faces are present is not a reliable guide to the absolute orientation of the polar c axis. For example, the Sm crystal (Table 1) exhibited only the $\{11\bar{1}\}$ and $\{131\}$ faces, while the Gd crystal showed $\{13\bar{1}\}$ and three each of $\{111\}$ and $\{11\bar{1}\}$. Similar variation occurred among many other crystals we have examined. The absolute setting used here may be identified by the intensity inequalities $004 > 00\bar{4}$, $008 < 00\bar{8}$.

Structure analysis

The trial structures for refinement were derived directly or indirectly from Koetzle's (1978) coordinates for the Sm salt, but modified by various transformations of setting. We defined the origin by holding the lanthanoid atom at a fixed z coordinate. Scattering factors, including anomalous-scattering effects for all atoms except H, were taken from *International Tables for X-ray Crystallography* (1974) for Ln^{3+}, Na^+, $O^{\frac{1}{2}-}$ (edta O atoms), for neutral C, N, and O (water O atoms), and for spherical bonded H. For each rare-earth atom f'' was determined as an adjustable parameter. Only 20 of the 28 H atoms were included in the calculations; those on water molecules $W(2)$ to $W(5)$ (those with the largest apparent thermal motion) were omitted. For the Pr and Sm structures the H coordinates were derived from the Sm neutron diffraction values (Koetzle, 1978). Isotropic thermal parameters, constrained to be equal for each pair of H atoms bonded to the same C or O atom, were refined using the Pr data. The same values were used without change in the refinement of the Sm structure. For the Gd structure the coordinates of the same 20 H atoms were adjusted in the refinement, but with restraints to hold distances close to $C-H = 1.00$, $O-H = 0.90$, $H-H = 1.63$ (carbon H), and $H-H = 1.47$ Å (water H), all ±0.05 Å. Again the isotropic thermal parameters were constrained to be equal by pairs. All non-hydrogen atoms were assigned anisotropic thermal parameters. In the final cycles whose results are reported here only the non-hydrogen atoms were refined, but the parameters changed little from the earlier cycles where H parameters were adjusted. Zero weight was assigned to reflections weaker than 1σ; for others $w = [\sigma(F)]^{-2}$; $\sigma(F)$ was derived from $\sigma(F^2) = [S^2 + (pF^2)^2]^{1/2}$ where S^2 is the variance due to counting statistics and p is listed in Table 1. In the Gd refinement zero weight was also assigned to the four lowest-angle reflections, and a small extinction correction was applied; the latter affected no structure factor more than 1%.

Table 1. *Diffraction data for* $Na[Ln(edta)(H_2O)_3].-5H_2O$ *compounds*

Ln	Pr	Sm	Gd
Faces	16	8	10
Volume (mm³)	6.32×10^{-4}	1.12×10^{-3}	4.93×10^{-4}
Absorption correction	1·15–1·22	1·21–1·30	1·17–1·36
p	0·04	0·02	0·025
Reflections measured	4012	3991	7772
Unique reflections, $F^2 > \sigma$	3449	3368	3386
Maximum $(\sin \theta)/\lambda$ (Å⁻¹)	0·596	0·596	0·594
$R = \sum |\Delta I|/\sum |F_o|$	0·037	0·030	0·024
$R_w = (\sum w\Delta I^2/\sum wF_o^2)^{1/2}$	0·036	0·029	0·025
f'', experimental (e atom⁻¹)	2·87 (11)	3·64 (10)	3·91 (9)
f'', calculated (e atom⁻¹)	2·82*	3·442†	3·904†

* Cromer & Liberman (1981).
† Cromer & Liberman (1970).

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{8}{3} \pi^2 \text{ trace } \tilde{U}.$$

	x	y	z	B_{eq} (Å^2)
Na[Pr(edta)(H$_2$O)$_3$].5H$_2$O				
Pr	0·08342 (2)	0·15424 (1)	0	1·670 (7)
Na	0·13665 (18)	0·13164 (10)	0·3162 (3)	3·8 (1)
O(1)	0·0977 (3)	0·18278 (14)	0·1826 (4)	2·7 (1)
O(2)	−0·0296 (3)	0·16991 (16)	0·0711 (5)	3·0 (1)
O(3)	0·2067 (3)	0·16902 (15)	0·0279 (4)	2·5 (1)
O(4)	0·0186 (3)	0·16490 (14)	−0·1692 (4)	2·2 (1)
O(5)	0·1061 (4)	0·23178 (18)	0·2947 (5)	5·1 (2)
O(6)	−0·0968 (4)	0·21156 (21)	0·1514 (6)	5·9 (2)
O(7)	0·3122 (3)	0·17571 (19)	−0·0344 (5)	4·1 (2)
O(8)	0·0117 (3)	0·17261 (18)	−0·3525 (4)	3·2 (2)
O(9)	0·0015 (3)	0·09753 (12)	−0·0142 (4)	2·8 (1)
O(10)	0·1370 (3)	0·10858 (16)	−0·1280 (5)	2·8 (2)
O(11)	0·1353 (3)	0·10426 (14)	0·1217 (4)	2·4 (1)
N(1)	0·0579 (3)	0·22827 (15)	0·0068 (6)	2·6 (1)
N(2)	0·1496 (3)	0·19316 (18)	−0·1617 (5)	2·1 (2)
C(1)	0·0792 (4)	0·24674 (28)	−0·0955 (7)	2·8 (2)
C(2)	0·1489 (4)	0·23358 (21)	−0·1336 (6)	2·9 (2)
C(3)	0·0983 (6)	0·24401 (26)	0·1033 (8)	3·8 (3)
C(4)	0·1008 (4)	0·21770 (22)	0·2022 (7)	3·0 (2)
C(5)	−0·0161 (5)	0·23416 (22)	0·0235 (7)	3·8 (3)
C(6)	−0·0484 (5)	0·20290 (26)	0·0879 (7)	3·6 (2)
C(7)	0·2216 (4)	0·18098 (23)	−0·1641 (7)	2·7 (2)
C(8)	0·2494 (4)	0·17531 (22)	−0·0482 (6)	2·6 (2)
C(9)	0·1174 (4)	0·18586 (23)	−0·2698 (6)	2·7 (2)
C(10)	0·0422 (4)	0·17362 (19)	−0·2624 (7)	2·4 (2)
W(1)	0·0625 (3)	0·03971 (16)	0·1031 (5)	4·1 (2)
W(2)	0·1478 (5)	0·09818 (23)	0·5436 (9)	9·4 (4)
W(3)	0·1153 (7)	0·17824 (25)	0·4508 (7)	10·1 (4)
W(4)	0·0187 (6)	0·11154 (33)	0·3155 (11)	11·5 (4)
W(5)	0·2646 (8)	0·21580 (41)	0·5646 (10)	15·7 (6)

	x	y	z	B_{eq} (Å^2)
Na[Sm(edta)(H$_2$O)$_3$].5H$_2$O				
Sm	0·08333 (1)	0·15487 (1)	0	1·397 (6)
Na	0·13752 (16)	0·13227 (9)	0·31437 (26)	3·42 (9)
O(1)	0·0972 (2)	0·18234 (12)	0·1821 (4)	2·3 (1)
O(2)	−0·0284 (2)	0·16881 (13)	0·0724 (4)	2·4 (1)
O(3)	0·2053 (2)	0·16902 (13)	0·0302 (3)	2·2 (1)
O(4)	0·0181 (2)	0·16416 (13)	−0·1658 (4)	1·9 (1)
O(5)	0·1057 (3)	0·23154 (15)	0·2947 (4)	3·9 (2)
O(6)	−0·0985 (2)	0·20989 (17)	0·1530 (5)	4·9 (2)
O(7)	0·3114 (2)	0·17648 (17)	−0·0301 (4)	3·6 (2)
O(8)	0·0103 (3)	0·17186 (16)	−0·3489 (4)	3·0 (1)
O(9)	0·0028 (2)	0·09809 (11)	−0·0137 (4)	2·1 (1)
O(10)	0·1362 (2)	0·10966 (14)	−0·1254 (4)	2·5 (1)
O(11)	0·1335 (2)	0·10553 (13)	0·1213 (4)	2·2 (1)
N(1)	0·0566 (3)	0·22792 (13)	0·0055 (6)	2·2 (1)
N(2)	0·1493 (3)	0·19304 (16)	−0·1598 (4)	1·8 (1)
C(1)	0·0783 (4)	0·24753 (25)	−0·0964 (7)	2·5 (2)
C(2)	0·1479 (4)	0·23391 (20)	−0·1333 (6)	2·5 (2)
C(3)	0·0953 (5)	0·24365 (23)	0·1027 (7)	3·0 (2)
C(4)	0·0989 (4)	0·21696 (20)	0·2011 (6)	2·6 (2)
C(5)	−0·0175 (4)	0·23309 (20)	0·0225 (6)	3·2 (2)
C(6)	−0·0499 (4)	0·20187 (21)	0·0886 (6)	2·8 (2)
C(7)	0·2214 (3)	0·18091 (20)	−0·1605 (6)	2·2 (2)
C(8)	0·2488 (4)	0·17521 (19)	−0·0453 (5)	2·3 (2)
C(9)	0·1168 (3)	0·18580 (20)	−0·2688 (5)	2·1 (2)
C(10)	0·0428 (3)	0·17300 (17)	−0·2609 (6)	1·9 (2)
W(1)	0·0633 (3)	0·04011 (14)	0·1034 (4)	3·4 (1)
W(2)	0·1482 (4)	0·09850 (19)	0·5497 (7)	7·6 (3)
W(3)	0·1182 (5)	0·17880 (21)	0·4537 (5)	8·6 (3)
W(4)	0·0200 (4)	0·11310 (28)	0·3313 (9)	10·8 (4)
W(5)	0·2604 (6)	0·21434 (34)	0·5609 (8)	15·5 (5)

Table 2 (*cont.*)

	x	y	z	B_{eq} (Å^2)
Na[Gd(edta)(H$_2$O)$_3$].5H$_2$O				
Gd	0·08251 (1)	0·15503 (1)	0	1·420 (5)
Na	0·13651 (14)	0·13233 (7)	0·31280 (22)	3·82 (7)
O(1)	0·0964 (2)	0·18200 (10)	0·1811 (3)	2·3 (1)
O(2)	−0·0289 (2)	0·16839 (11)	0·0723 (3)	2·5 (1)
O(3)	0·2033 (2)	0·16881 (11)	0·03138 (27)	2·3 (1)
O(4)	0·0176 (2)	0·16431 (10)	−0·16449 (29)	1·80 (9)
O(5)	0·1059 (3)	0·23117 (13)	0·2938 (3)	4·1 (1)
O(6)	−0·1003 (3)	0·20893 (15)	0·1512 (4)	5·4 (2)
O(7)	0·3109 (2)	0·17657 (13)	−0·0275 (3)	3·6 (1)
O(8)	0·0087 (2)	0·17149 (13)	−0·3471 (3)	3·1 (1)
O(9)	0·0034 (2)	0·09854 (9)	−0·0137 (3)	2·27 (9)
O(10)	0·1348 (2)	0·11013 (12)	−0·1243 (3)	2·5 (1)
O(11)	0·1317 (2)	0·10593 (11)	0·1210 (3)	2·2 (1)
N(1)	0·0562 (2)	0·22775 (11)	0·0077 (4)	2·2 (1)
N(2)	0·1485 (2)	0·19319 (13)	−0·1586 (4)	1·8 (1)
C(1)	0·0769 (3)	0·24709 (19)	−0·0953 (5)	2·3 (2)
C(2)	0·1465 (3)	0·23404 (17)	−0·1328 (5)	2·7 (2)
C(3)	0·0942 (4)	0·24353 (19)	0·1034 (6)	3·1 (2)
C(4)	0·0980 (3)	0·21683 (16)	0·2010 (5)	2·2 (1)
C(5)	−0·0194 (3)	0·23265 (16)	0·0242 (5)	3·1 (2)
C(6)	−0·0513 (3)	0·20128 (18)	0·0886 (5)	2·8 (2)
C(7)	0·2208 (3)	0·18104 (17)	−0·1597 (5)	2·5 (1)
C(8)	0·2477 (3)	0·17527 (16)	−0·0436 (4)	2·3 (1)
C(9)	0·1161 (3)	0·18532 (15)	−0·2663 (5)	2·4 (1)
C(10)	0·0413 (2)	0·17304 (13)	−0·2583 (5)	2·0 (1)
W(1)	0·0625 (2)	0·03988 (12)	0·1024 (4)	3·7 (1)
W(2)	0·1492 (4)	0·09816 (18)	0·5551 (7)	8·2 (2)
W(3)	0·1187 (5)	0·17871 (19)	0·4544 (5)	9·0 (3)
W(4)	0·0207 (4)	0·11274 (28)	0·3329 (9)	12·5 (4)
W(5)	0·2579 (6)	0·21439 (42)	0·5607 (8)	18·3 (6)

Final values of R, R_w and f'' are listed in Table 1. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.*

Discussion

With R values in the range 0·024 to 0·037 this work achieved its primary objective of obtaining parameters which fit X-ray diffraction intensities accurately enough to be used to analyze our synchrotron-radiation experiments cited above. A second result is the experimental values of f'' for these three rare-earth elements for Mo $K\alpha$ radiation (Table 1). Like our earlier results for Cs (Templeton & Templeton, 1978) and Co and Cl (Templeton, Zalkin, Ruben & Templeton, 1979) the agreement with the values calculated by Cromer & Liberman (1970, 1981) is excellent for this wavelength remote from the absorption edges. This is in contrast to huge differences observed in the immediate regions of absorption edges. In this analysis

* Lists of H-atom parameters, anisotropic thermal parameters, interatomic distances and angles, and structure factors for the three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36820 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

we assumed that the theoretical values for f' were correct in order to avoid difficult-to-analyze systematic errors which might result from strong coupling of f' with thermal parameters, errors in absorption corrections, and other effects correlated with diffraction angle. A test refinement of the Gd data, in which both f' and f'' as well as all the structural parameters were varied, yielded $f'' = 3.87$ (9) e atom^{-1}, hardly different from the value cited above, and $f' = -1.11$ (17) e atom^{-1}, different by about 3σ from Cromer & Liberman's value.

In structure determinations of non-centrosymmetric crystals, particularly polar ones, it is important to avoid inversion twinning, or else consider it explicitly in the calculations (Templeton & Templeton, 1978; Rietz, Zalkin, Templeton, Edelstein & Templeton, 1978; Rogers, 1981). When scattering factors are being measured as in the present work it is crucial to avoid twinning. For this reason we adopted these edta crystals for this work only after much labor failed to achieve satisfactory crystals of any lanthanide tartrate salts. With optically pure salts of tartaric acid the intrinsic chirality makes inversion twinning impossible. Fortunately, inversion twinning (if it occurs at all) is rare in these edta salts, at least in well formed crystals such as we have selected. The good agreement of measured and theoretical f'' values cited above indicates it was absent in these three crystals. Nor was any evidence of it detected in any of the several other crystals we have used in synchrotron-radiation experiments.

The crystal structure itself, which has already been described by earlier authors cited above, needs little comment here. The principal differences among these isomorphous crystals are the result of the different sizes of the lanthanoid ions. The neighbor distances of these ions are listed in Table 3 with corresponding values reported by Nassimbeni *et al.* (1979) for the Dy compound. Corresponding distances for our three structures trend downward consistently with increasing atomic number, with an average decrease of 0.061 Å from Pr to Gd; the ionic radii calculated from oxide and chloride structures (Templeton & Dauben, 1954) decrease 0.075 Å in the same interval. The distances for the Dy salt do not fit this pattern. Nassimbeni *et al.* (1979) do not mention anomalous scattering or the determination of the absolute polarity of their crystal. This fact suggests that the polar dispersion error may have occurred (Ueki, Zalkin & Templeton, 1966; Cruickshank & McDonald, 1967). If the z coordinate of Dy is changed to 0.006 (a change of about 0.07 Å) distances are calculated (Table 3) which are much more consistent with our values. This change is more than one would estimate if anomalous scattering ($f'' = 4.4$ e atom^{-1} for Dy at Mo $K\alpha$) had simply been neglected, but is a reasonable amount if the refinement had been performed with the correct f'' but the

configuration reverse to that of the specimen. Whatever the facts, this example illustrates again the need for care with anomalous-scattering effects in polar space groups.

There is nothing novel about the bond structure of the edta moiety, but the redundancy of these three determinations permits averaging of from 3 to 12 independent measurements to obtain accurate average values for each chemical type of bond distance and angle. These averages are shown in Fig. 1.

The large and highly anisotropic thermal parameters for some of the water molecules (not including any of those coordinated to rare-earth atoms) evidently indicate some disorder of location and partial occupancy of sites. This aspect of the structure has been under investigation by neutron diffraction at low temperature by Koetzle & Engel (1981). For our purposes the description by highly anisotropic thermal parameters seemed to be sufficient, and we have not attempted to resolve the details of this disorder.

Table 3. *Neighbor distances* (Å) *for rare-earth ions*

Ln	$_{59}$Pr	$_{62}$Sm	$_{64}$Gd	$_{66}$Dy^a	$_{66}$Dy^b
Ln–O(1)	2.453 (5)	2.429 (4)	2.409 (4)	2.464 (14)	2.397
–O(2)	2.441 (5)	2.401 (5)	2.381 (4)	2.396 (15)	2.368
–O(3)	2.495 (5)	2.458 (4)	2.425 (4)	2.420 (14)	2.408
–O(4)	2.442 (5)	2.400 (4)	2.381 (3)	2.285 (15)	2.346
Ave.^{d}	2.458	2.422	2.399	2.391^c	2.380
Ln–O(9)	2.592 (5)	2.565 (4)	2.531 (3)	2.553 (12)	2.559
–O(10)	2.485 (5)	2.442 (5)	2.416 (4)	2.351 (16)	2.397
–O(11)	2.531 (5)	2.490 (5)	2.469 (4)	2.483 (14)	2.440
Ave.^{e}	2.536	2.499	2.472	2.462	2.465
Ln–N(1)	2.696 (5)	2.653 (5)	2.632 (4)	2.642 (16)	2.637
–N(2)	2.731 (6)	2.693 (5)	2.677 (4)	2.614 (17)	2.665
Ave.	2.714	2.673	2.655	2.628	2.651

Notes: (a) Nassimbeni, Wright, van Niekerk & McCallum (1979); (b) recalculated as described in the text; (c) reported incorrectly as 2.319 Å, (d) Ln–O(edta); (e) Ln–O(water).
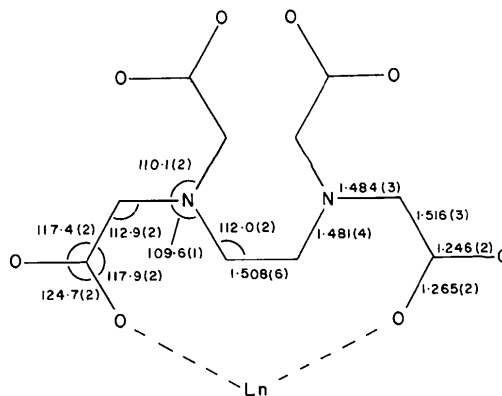

Fig. 1. Bond distances (Å) and angles (°) in the edta moiety, averaged for the 3 to 12 chemically equivalent bonds in the Pr, Sm and Gd salts.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & LIBERMAN, D. (1981). *Acta Cryst.* A**37**, 267–268.

CRUICKSHANK, D. W. J. & MCDONALD, W. S. (1967). *Acta Cryst.* **23**, 9–11.

HOARD, J. L., LEE, B. & LIND, M. D. (1965). *J. Am. Chem. Soc.* **87**, 1612–1613.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KOETZLE, T. F. (1978). Private communication.

KOETZLE, T. F. & ENGEL, D. W. (1981). Private communication.

KOETZLE, T. F. & HAMILTON, W. C. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 489–502. Copenhagen: Munksgaard.

NASSIMBENI, L. R., WRIGHT, M. R. W., VAN NIEKERK, J. C. & MCCALLUM, P. A. (1979). *Acta Cryst.* B**35**, 1341–1345.

RIETZ, R. R., ZALKIN, A., TEMPLETON, D. H., EDELSTEIN, N. M. & TEMPLETON, L. K. (1978). *Inorg. Chem.* **17**, 653–658.

ROGERS, D. (1981). *Acta Cryst.* A**37**, 734–741.

TEMPLETON, D. H. & DAUBEN, C. H. (1954). *J. Am. Chem. Soc.* **76**, 5237–5239.

TEMPLETON, D. H., ZALKIN, A., RUBEN, H. W. & TEMPLETON, L. K. (1979). *Acta Cryst.* B**35**, 1608–1613.

TEMPLETON, L. K. & TEMPLETON, D. H. (1978). *Acta Cryst.* A**34**, 368–371.

TEMPLETON, L. K., TEMPLETON, D. H. & PHIZACKERLEY, R. P. (1980). *J. Am. Chem. Soc.* **102**, 1185–1186.

TEMPLETON, L. K., TEMPLETON, D. H., PHIZACKERLEY, R. P. & HODGSON, K. O. (1982). *Acta Cryst.* A**38**, 74–78.

UEKI, T., ZALKIN, A. & TEMPLETON, D. H. (1966). *Acta Cryst.* **20**, 836–841.

Structure du Perchlorate de μ-(Méthyl-9 adéninato-N^1,N^6)-bis[méthylmercure(II)]

PAR MARC J. OLIVIER ET ANDRÉ L. BEAUCHAMP*

Département de Chimie, Université de Montréal, CP 6210, Succ. A, Montréal, Québec, Canada H3C 3V1

Abstract

$C_8H_{12}Hg_2N_5^+.ClO_4^-$, monoclinic, space group $P2_1/c$, $a = 10.903$ (5), $b = 12.690$ (10), $c = 11.479$ (7) Å, $\beta = 115.32$ (6)°, $V = 1435.6$ Å^3, $M_r = 678.8$, $Z = 4$, $D_c = 3.14$ Mg m^{-3}. The structure was refined on 1489 independent nonzero reflections to an R factor of 0.036. One of the CH_3Hg groups is coordinated to N(1), whereas the other group has substituted an amino H. The CH_3Hg units are found in the less sterically hindered *transoid* orientation. Centrosymmetrically related $[(CH_3Hg)_2(mad)]^+$ cations are packed parallel with a separation of ~3.5 Å in the cell. They interact with the ClO_4^- ions through hydrogen bonds involving the remaining amino H and secondary Hg–O

Introduction

Le présent travail s'inscrit dans le cadre d'une étude systématique visant à déterminer les affinités relatives des différents sites de complexation de l'adénine pour les métaux lourds. L'utilisation du dérivé méthylé à l'atome N(9) empêche l'interaction du métal avec cette position, qui est bloquée par le lien rattachant l'adénine à la chaîne principale dans les acides nucléiques. Nous avons déjà montré que l'ion CH_3Hg^+ se fixe dans un premier temps sur le doublet libre de l'atome N(1) (Olivier & Beauchamp, 1980). Un second ion CH_3Hg^+ peut se lier sans départ de proton, sans doute en N(7) (Savoie, Poirier, Prizant & Beauchamp, 1981), si le milieu est franchement acide, tandis que la complexation s'accompagne d'un départ de proton en milieu neutre ou peu acide. Le présent travail avait pour but de préciser les sites de coordination dans le composé $[(CH_3Hg)_2(mad)]ClO_4†$ isolé en milieu peu acide. Une description sommaire de cette structure a été présentée (Prizant, Olivier, Rivest & Beauchamp, 1979).

---

† Méthyl-9 adénine neutre = Hmad, espèce anionique obtenue par départ d'un proton = mad.

* Auteur auquel la correspondance devra être adressée.