

Fig. 3. ORTEP (Johnson, 1965) drawing of the asymmetric unit in $\text{GaPO}_4\cdot 14$ (see Tables 1 and 2). Hydrogen atoms [H(1)–H(3)] are hydrogen bonded (dotted lines) to oxygen atoms of the framework.

Template. The isopropylamine molecule is hydrogen bonded to the framework (Fig. 3) via N–H...O linkages. The geometries of these are as follows: N–H(1)...O(10), 2.29 (3) Å, 123 (5)°; N–H(2)...O(6), 1.99 (2) Å, 166 (5)°; N–H(3)...O(17), 2.18 (2) Å, 166 (5)°; the first figure quoted is the H...O distance and the second the N–H...O angle. This hydrogen-bonding scheme serves to anchor the amine group, which has a low thermal parameter

relative to those for the carbon atoms (Table 1 and Fig. 3).

References

- BENNETT, J. M., COHEN, P. M., ARTIOLI, G., PLUTH, J. J. & SMITH, J. V. (1985). *J. Inorg. Chem.* **24**, 188–193.
 BENNETT, J. M., COHEN, J. P., FLANIGEN, E. M., PLUTH, J. J. & SMITH, J. V. (1983). *Am. Chem. Soc. Symp. Ser.* **218**, 109–118.
 BENNETT, J. M. & SMITH, J. V. (1985). *Z. Kristallogr.* In the press.
 BLOSS, F. D. (1971). *Crystallography and Crystal Chemistry*. New York: Holt, Rinehart and Winston.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KNIEP, R. & MOOTZ, D. (1973). *Acta Cryst.* **B29**, 2292–2294.
 KNIEP, R., MOOTZ, D. & VEGAS, A. (1977). *Acta Cryst.* **B33**, 263–265.
 MOONEY-SLATER, R. C. L. (1966). *Acta Cryst.* **20**, 526–534.
 PARISE, J. B. (1984a) *International Symposium on Zeolites, Protoroz.* Amsterdam: Elsevier Scientific. In the press.
 PARISE, J. B. (1984b). *Acta Cryst.* **C40**, 1641–1642.
 PARISE, J. B. (1984c). *J. Chem. Soc. Chem. Commun.* **21**, 1449–1450.
 PARISE, J. B. (1985a). *J. Chem. Soc. Chem. Commun.* **9**, 606–607.
 PARISE, J. B. (1985b). *J. Inorg. Chem.* **24**, 4312–4316.
 PARISE, J. B. (1986). *Acta Cryst.* **C42**, 144–147.
 PARISE, J. B. & DAY, C. S. (1985). *Acta Cryst.* **C41**, 515–517.
 SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
 WILSON, T., LOK, B. M. & FLANIGEN, E. M. (1982). US patent no. 4 310 440.
 WILSON, T., LOK, B. M., MESSINA, C. A., CANNAN, T. R. & FLANIGEN, E. M. (1982). *J. Am. Chem. Soc.* **104**, 1146–1147.

Acta Cryst. (1986). **C42**, 673–677

Structural Comparison of (*o*-Phenylenediaminetetraacetato)zinc(II) with its Protonated Complex, $X_2\text{ZnC}_{14}\text{H}_{12}\text{N}_2\text{O}_8\cdot n\text{H}_2\text{O}$ ($X = \text{K}$ or H)

BY SHIGEKI AZUMA, NORIYUKI NAKASUKA* AND MOTOHARU TANAKA*

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

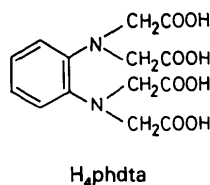
(Received 7 November 1985; accepted 12 December 1985)

Abstract. (1) $X = \text{K}$, $n = 3$, $M_r = 533.9$, monoclinic, $P2_1/a$, $a = 24.140$ (3), $b = 8.551$ (1), $c = 9.684$ (1) Å, $\beta = 97.11$ (1)°, $V = 1983.7$ (4) Å³, $Z = 4$, $D_m = 1.780$, $D_x = 1.788$ g cm⁻³, $\mu = 59.9$ cm⁻¹, $F(000) = 1088$, final $R = 0.037$ for 3113 observed reflections. (2) $X = \text{H}$, $n = 2$, $M_r = 439.7$, triclinic, $P\bar{1}$, $a = 12.851$ (3), $b = 15.366$ (7), $c = 9.583$ (2) Å, $\alpha = 103.48$ (4), $\beta =$

89.28 (2), $\gamma = 108.67$ (4)°, $V = 1739$ (1) Å³, $Z = 4$, $D_m = 1.682$, $D_x = 1.678$ g cm⁻³, $\mu = 23.2$ cm⁻¹, $F(000) = 904$, final $R = 0.046$ for 5469 observed reflections. For both cases $\lambda(\text{Cu } K\alpha) = 1.5417$ Å, $T = 293$ K. In the potassium complex ($X = \text{K}$), the zinc ion is hexacoordinate but the coordination environment deviates markedly from O_h . In the diprotonated complex ($X = \text{H}$), a coordinated carboxylate O is replaced by a water molecule and the coordination polyhedron retrieves the octahedral geometry.

* Authors to whom correspondence should be addressed.

Introduction. Protonation of metal chelates leads to the dissociation of a coordinate bond, followed by the substitution of a solvent molecule for a donor atom bound to the central metal ion. This process may be accompanied by a partial release of strains applied to a chelate ring, especially in complexes of multidentate ligands such as aminopolycarboxylates. Considerable distortion from the octahedral geometry has been observed for *o*-phenylenediaminetetraacetato (phdta, *L*) complexes of cobalt(II) (McCandlish, Michael, Neal, Lingafelter & Rose, 1978) and manganese(II) (Nakasuka, Azuma, Katayama, Honda, Tanaka & Tanaka, 1985), since this ligand is less flexible. Therefore it is thought of interest to compare the molecular structure of a normal 1:1 complex with that of its protonated complex for this ligand.



Experimental. (1) K₂ZnL·3H₂O: Transparent, short prismatic crystal, prepared in a way similar to that described for the Mn^{II}-phdta complex (Nakasuka, Azuma, Katayama, Honda, Tanaka & Tanaka, 1985), 0.15 × 0.18 × 0.20 mm. Elemental analysis: calcd for C₁₄H₁₈K₂N₂O₁₁Zn: C 31.50, N 5.25, H 3.40%; found: C 31.16, N 5.21, H 3.26%. Total of 3787 reflections measured, 2θ_{max} = 126°, -28 ≤ h ≤ 28, 0 ≤ k ≤ 10, 0 ≤ l ≤ 11, R_{int} = 0.022. Transmission factors 0.31 to 0.42, R = 0.037, wR = 0.037, S = 2.38, w = 1/σ²(F²), (Δ/σ)_{max} = 0.12 for B₃₁ of C(60) (except H atoms), Δρ_{max} = 0.35 e Å⁻³. (2) H₂ZnL(H₂O)·H₂O: Well formed, almost colorless, transparent, stout prismatic crystal, obtained similarly but without adding KOH, 0.30 × 0.10 × 0.20 mm. Elemental analysis: calcd for C₁₄H₁₈N₂O₁₀Zn: C 38.24, N 6.37, H 4.13%; found: C 38.06, N 6.31, H 4.06%. Total of 5469 reflections measured, 2θ_{max} = 126°, -15 ≤ h ≤ 15, -18 ≤ k ≤ 18, 0 ≤ l ≤ 11, R_{int} = 0.022. Transmission factors 0.50 to 0.79, R = 0.046, wR = 0.058, S = 2.69, weights as for (1), (Δ/σ)_{max} = 0.20 for x of O(12), Δρ_{max} = 0.99 e Å⁻³.

D_m by flotation in C₆H₅CH₃/C₂H₄Br₂. Rigaku AFC-5A automated four-circle diffractometer. Cell dimensions from 20 selected reflections with 29 < θ < 31°. Three standard reflections after every 100 reflections, no variation in intensity. Structure solved by the Monte Carlo direct method (Furusaki, 1979) with the aid of MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) using 3113

(1) or 5469 (2) non-zero unique reflections [*I* > 3σ(*I*)], refined on *F*² by full-matrix least-squares program with analytical absorption correction (Katayama, Sakabe & Sakabe, 1972). Non-H atoms assigned anisotropic temperature factors. All H atoms located from difference Fourier map and refined with isotropic temperature factors equivalent to those for bonded atoms. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). ORTEP (Johnson, 1965) employed for drawing molecular structure and PLUTO78 (Motherwell, 1978) for crystal-structure projection. All calculations made on a FACOM M-382 computer at the Computation Center, Nagoya University. Elemental analysis was performed by the micro-analytical section at the Faculty of Agriculture, Nagoya University.

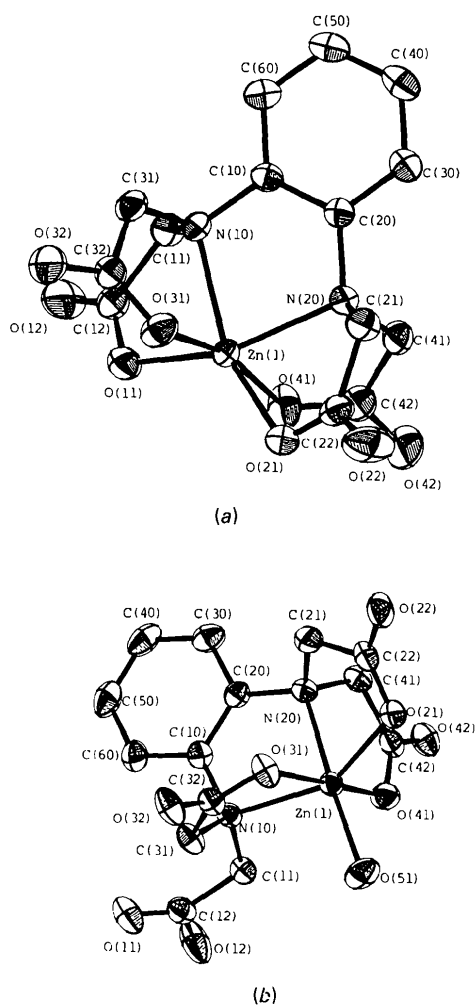


Fig. 1. ORTEP plots of (a) [Zn(phdta)]²⁻ and (b) [Zn(H₂phdta)(H₂O)] showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

$$B_{eq} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
(i) $K_2ZnL \cdot 3H_2O$				
Zn(1)	0.37304 (1)	0.18877 (4)	0.70164 (3)	1.88 (1)
K(2)	0.20710 (3)	0.82393 (8)	1.00707 (7)	3.49 (1)
K(3)	0.70430 (3)	0.44534 (7)	0.65317 (7)	3.43 (1)
C(20)	0.47154 (10)	-0.03027 (29)	0.75174 (24)	1.98 (5)
C(10)	0.49576 (10)	0.11210 (29)	0.72276 (24)	2.02 (5)
C(60)	0.55384 (11)	0.12152 (34)	0.72452 (27)	2.59 (5)
C(50)	0.58696 (11)	-0.00895 (37)	0.75807 (29)	2.89 (6)
C(40)	0.56283 (12)	-0.14940 (35)	0.79094 (29)	2.98 (6)
C(30)	0.50515 (11)	-0.15981 (32)	0.78861 (27)	2.59 (5)
N(10)	0.46087 (8)	0.24857 (24)	0.69434 (21)	1.93 (4)
C(31)	0.47447 (11)	0.37711 (33)	0.79663 (30)	2.61 (6)
C(32)	0.42715 (11)	0.41687 (31)	0.88089 (27)	2.45 (5)
O(31)	0.38735 (8)	0.32002 (25)	0.87965 (20)	3.01 (4)
O(32)	0.43148 (9)	0.54017 (27)	0.94873 (26)	3.93 (5)
C(11)	0.45930 (11)	0.30547 (33)	0.54965 (27)	2.49 (5)
C(12)	0.40834 (11)	0.41157 (31)	0.51091 (27)	2.54 (5)
O(11)	0.36568 (8)	0.38829 (23)	0.57522 (21)	2.90 (4)
O(12)	0.41055 (10)	0.50875 (31)	0.41836 (28)	4.39 (6)
N(20)	0.41091 (8)	-0.04097 (24)	0.74425 (21)	2.00 (4)
C(21)	0.39329 (11)	-0.07937 (35)	0.88067 (29)	2.66 (6)
C(22)	0.33288 (10)	-0.02901 (32)	0.89007 (28)	2.59 (5)
O(21)	0.31220 (7)	0.07732 (23)	0.80877 (21)	2.90 (4)
O(22)	0.30891 (9)	-0.09177 (35)	0.98064 (27)	4.76 (6)
C(41)	0.38585 (12)	-0.14768 (31)	0.63309 (31)	2.72 (5)
C(42)	0.34024 (11)	-0.07261 (34)	0.53051 (28)	2.73 (5)
O(41)	0.33699 (10)	0.07374 (25)	0.52625 (23)	3.68 (5)
O(42)	0.31047 (10)	-0.16301 (28)	0.45266 (27)	4.34 (6)
O(1)	0.79129 (11)	0.25667 (28)	0.27657 (26)	3.93 (6)
O(2)	0.27390 (11)	0.46737 (36)	0.72762 (28)	4.45 (6)
O(3)	0.16148 (12)	0.10939 (34)	0.90707 (31)	4.70 (6)
(ii) $H_2ZnL(H_2O)_2 \cdot H_2O$				
Zn(1)	0.45220 (3)	0.19013 (3)	0.38014 (4)	2.20 (1)
Zn(1')	0.80024 (3)	0.17628 (3)	0.88912 (4)	2.28 (1)
O(31')	0.82415 (16)	0.27414 (15)	1.09578 (20)	2.92 (5)
O(31)	0.50455 (16)	0.27794 (16)	0.59331 (21)	3.04 (5)
O(21')	0.66730 (16)	0.22522 (15)	0.85612 (22)	3.00 (6)
O(42')	0.82718 (18)	0.08308 (18)	0.46656 (22)	3.74 (6)
O(32)	0.44518 (18)	0.32139 (18)	0.80808 (21)	3.48 (6)
O(41)	0.38985 (17)	0.11256 (14)	0.17779 (21)	2.81 (5)
O(11)	0.07755 (17)	0.17387 (18)	0.56502 (23)	3.73 (6)
O(61')	0.49941 (21)	0.06720 (19)	0.70922 (25)	3.57 (6)
O(21)	0.62400 (17)	0.23754 (15)	0.35072 (23)	3.07 (6)
O(41')	0.80283 (20)	0.08949 (15)	0.69636 (22)	3.43 (6)
O(51)	0.43163 (22)	0.07407 (17)	0.44920 (27)	3.72 (7)
O(22')	0.64526 (17)	0.36634 (15)	0.87901 (24)	3.36 (6)
O(22)	0.75899 (17)	0.37680 (16)	0.38263 (25)	3.61 (6)
O(42)	0.37967 (17)	0.12436 (16)	-0.04772 (21)	3.23 (6)
O(61)	0.69657 (23)	0.08543 (19)	0.24685 (25)	4.13 (7)
O(51')	0.73402 (25)	0.06579 (18)	0.97068 (28)	4.33 (7)
O(32')	0.91164 (18)	0.31196 (18)	1.31099 (22)	3.62 (6)
O(11')	1.16787 (27)	0.16410 (28)	1.06516 (27)	7.30 (12)
O(12')	1.17704 (23)	0.08694 (23)	0.84409 (28)	5.44 (9)
O(12)	0.01381 (20)	0.07015 (21)	0.35595 (29)	4.47 (8)
N(10)	0.29941 (18)	0.22192 (16)	0.45908 (23)	2.14 (6)
N(10')	0.98036 (19)	0.20805 (17)	0.96091 (24)	2.45 (6)
N(20)	0.46873 (19)	0.30588 (16)	0.28443 (24)	2.22 (5)
N(20')	0.87622 (19)	0.28466 (16)	0.77732 (24)	2.32 (6)
C(22')	0.70004 (23)	0.31094 (21)	0.85413 (30)	2.60 (8)
C(20')	0.99319 (23)	0.32723 (20)	0.82071 (30)	2.52 (7)
C(32')	0.89808 (23)	0.27373 (21)	1.17478 (29)	2.53 (7)
C(21)	0.57813 (24)	0.37516 (22)	0.34115 (35)	2.84 (8)
C(32)	0.42938 (23)	0.28267 (20)	0.67252 (29)	2.50 (7)
C(42)	0.40647 (23)	0.15954 (21)	0.08095 (30)	2.59 (7)
C(20)	0.38086 (23)	0.34484 (19)	0.32448 (29)	2.30 (7)
C(42')	0.82664 (23)	0.12742 (23)	0.59297 (31)	2.89 (8)
C(12')	1.12652 (28)	0.12681 (24)	0.94513 (33)	3.53 (9)
C(11)	0.20488 (23)	0.13599 (21)	0.39134 (31)	2.46 (7)
C(10)	0.29911 (22)	0.30498 (20)	0.41057 (29)	2.28 (7)
C(30)	0.37744 (28)	0.42312 (22)	0.27775 (35)	3.21 (8)
C(10')	1.04334 (23)	0.29271 (21)	0.91366 (29)	2.57 (7)
C(41')	0.85197 (27)	0.23446 (24)	0.62178 (32)	3.03 (8)
C(21')	0.81907 (26)	0.35538 (22)	0.82178 (37)	3.12 (8)
C(31)	0.31039 (24)	0.23978 (24)	0.61739 (31)	2.83 (8)
C(22)	0.66040 (24)	0.32478 (22)	0.35867 (31)	2.82 (8)
C(31')	0.98038 (28)	0.22515 (27)	1.11951 (32)	3.19 (9)
C(11')	1.01434 (27)	0.12474 (23)	0.89037 (33)	3.10 (8)
C(41)	0.46556 (28)	0.26517 (22)	0.12666 (32)	2.88 (8)
C(30')	1.05543 (29)	0.40694 (24)	0.77343 (39)	3.69 (9)
C(60)	0.21712 (26)	0.34632 (22)	0.44797 (35)	3.11 (8)
C(12)	0.09356 (23)	0.13136 (21)	0.44962 (32)	2.72 (8)

Table 1 (cont.)

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(40)	0.29582 (29)	0.46264 (23)	0.31463 (38)	3.67 (9)
C(50)	0.21555 (29)	0.42395 (24)	0.39948 (39)	3.75 (9)
C(60')	1.15365 (27)	0.34084 (26)	0.96026 (38)	3.62 (9)
C(40')	1.16393 (29)	0.45258 (26)	0.82049 (44)	4.30 (10)
C(50')	1.21309 (30)	0.41993 (28)	0.91435 (44)	4.23 (10)

Table 2. Pertinent lengths (\AA) for the Zn-phdta complexes

(i) $K_2ZnL \cdot 3H_2O$			
(a) Zn(1)			
Zn(1)-N(10)	2.191 (2)	Zn(1)-N(20)	2.184 (3)
Zn(1)-O(31)	2.051 (2)	Zn(1)-O(21)	2.126 (2)
Zn(1)-O(11)	2.094 (2)	Zn(1)-O(41)	2.061 (2)
(b) Chelate rings etc.			
C(10)-N(10)	1.445 (3)	C(20)-N(20)	1.459 (3)
N(10)-C(31)	1.489 (3)	N(20)-C(21)	1.474 (4)
N(10)-C(11)	1.479 (3)	N(20)-C(41)	1.482 (3)
C(31)-C(32)	1.522 (4)	C(21)-C(22)	1.534 (4)
C(11)-C(12)	1.537 (4)	C(41)-C(42)	1.529 (4)
C(32)-O(31)	1.268 (3)	C(32)-O(32)	1.240 (4)
C(22)-O(21)	1.264 (3)	C(22)-O(22)	1.232 (4)
C(12)-O(11)	1.283 (3)	C(12)-O(12)	1.228 (4)
C(42)-O(41)	1.254 (4)	C(42)-O(42)	1.245 (4)
(ii) $H_2ZnL(H_2O)_2 \cdot H_2O$			
(a) Zn(1)			
Zn(1)-N(10)	2.252 (3)	Zn(1)-N(20)	2.136 (3)
Zn(1)-O(21)	2.130 (2)	Zn(1)-O(31)	2.148 (2)
Zn(1)-O(41)	2.043 (2)	Zn(1)-O(51)	1.983 (3)
(b) Zn(1')			
Zn(1')-N(10')	2.287 (3)	Zn(1')-N(20')	2.154 (2)
Zn(1')-O(21')	2.129 (3)	Zn(1')-O(31')	2.147 (2)
Zn(1')-O(41')	2.018 (2)	Zn(1')-O(51')	1.973 (3)
(c) Chelate rings etc.			
C(10)-N(10)	1.458 (4)	C(20)-N(20)	1.448 (4)
N(10)-C(11)	1.495 (3)	N(20)-C(21)	1.482 (3)
N(10)-C(31)	1.478 (4)	N(20)-C(41)	1.491 (4)
C(11)-C(12)	1.516 (4)	C(21)-C(22)	1.528 (5)
C(31)-C(32)	1.505 (4)	C(41)-C(42)	1.514 (4)
C(12)-O(11)	1.198 (4)	C(12)-O(12)	1.324 (3)
C(22)-O(21)	1.254 (4)	C(22)-O(22)	1.253 (3)
C(32)-O(31)	1.231 (4)	C(32)-O(32)	1.285 (3)
C(42)-O(41)	1.279 (4)	C(42)-O(42)	1.230 (3)
C(10')-N(10')	1.464 (4)	C(20')-N(20')	1.456 (4)
N(10')-C(11')	1.494 (5)	N(20')-C(21')	1.480 (5)
N(10')-C(31')	1.481 (4)	N(20')-C(41')	1.495 (4)
C(11')-C(12')	1.529 (5)	C(21')-C(22')	1.523 (4)
C(31')-C(32')	1.504 (5)	C(41')-C(42')	1.528 (5)
C(12')-O(11')	1.203 (4)	C(12')-O(12')	1.303 (5)
C(22')-O(21')	1.253 (4)	C(22')-O(22')	1.250 (4)
C(32')-O(31')	1.225 (4)	C(32')-O(32')	1.289 (3)
C(42')-O(41')	1.250 (4)	C(42')-O(42')	1.245 (3)

Discussion. Final atomic parameters are listed in Table 1.* The numbering system appears in Fig. 1, while bond lengths and bond angles may be found in Tables 2 and 3. The ligand is hexadentate in the normal complex ($K_2ZnL \cdot 3H_2O$), but pentadentate in the protonated complex [$H_2ZnL(H_2O)_2 \cdot H_2O$]. The two crystallographically independent diprotonated complexes have nearly equivalent structures. The two protons are

* Lists of structure factors, H-atom parameters, anisotropic thermal parameters, normal intermolecular distances, non-essential bond lengths and non-essential bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42757 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Pertinent angles (°) for the Zn-phdta complexes

(i) K₂ZnL·3H₂O

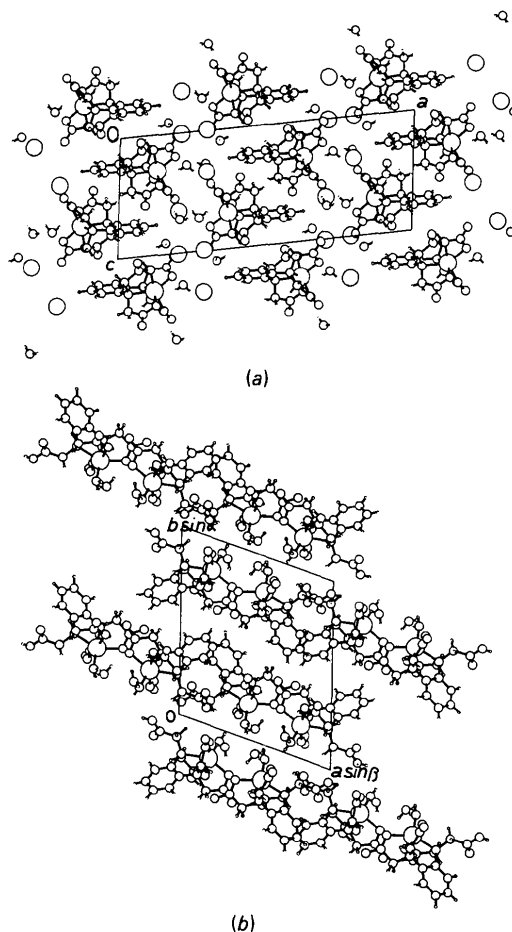
(a) Zn(1)			
N(10)—Zn(1)—N(20)	80.35 (7)	N(10)—Zn(1)—O(31)	80.56 (8)
N(10)—Zn(1)—O(21)	148.26 (7)	N(10)—Zn(1)—O(11)	78.64 (8)
N(10)—Zn(1)—O(41)	113.38 (9)	N(20)—Zn(1)—O(31)	108.10 (8)
N(20)—Zn(1)—O(21)	78.63 (7)	N(20)—Zn(1)—O(11)	147.79 (8)
N(20)—Zn(1)—O(41)	81.39 (8)	O(31)—Zn(1)—O(21)	83.69 (8)
O(31)—Zn(1)—O(11)	92.22 (8)	O(31)—Zn(1)—O(41)	164.73 (9)
O(21)—Zn(1)—O(11)	129.55 (7)	O(21)—Zn(1)—O(41)	86.62 (9)
O(11)—Zn(1)—O(41)	84.88 (8)		
(b) Chelate rings			
Zn(1)—N(10)—C(10)	110.4 (2)	N(10)—C(10)—C(20)	119.6 (2)
C(10)—C(20)—N(20)	119.2 (2)	C(20)—N(20)—Zn(1)	110.3 (2)
Zn(1)—N(10)—C(31)	106.6 (2)	N(10)—C(31)—C(32)	113.8 (2)
C(31)—C(32)—O(31)	117.9 (2)	C(32)—O(31)—Zn(1)	114.5 (2)
Zn(1)—N(10)—C(11)	101.3 (1)	N(10)—C(11)—C(12)	110.6 (2)
C(11)—C(12)—O(11)	117.1 (2)	C(12)—O(11)—Zn(1)	113.3 (2)
Zn(1)—N(20)—C(21)	102.1 (2)	N(20)—C(21)—C(22)	111.9 (2)
C(21)—C(22)—O(21)	118.0 (2)	C(22)—O(21)—Zn(1)	112.5 (2)
Zn(1)—N(20)—C(41)	107.0 (1)	N(20)—C(41)—C(42)	114.2 (2)
C(41)—C(42)—O(41)	118.5 (2)	C(42)—O(41)—Zn(1)	115.6 (2)
(c) Others			
C(10)—N(10)—C(31)	113.2 (2)	C(10)—N(10)—C(11)	113.1 (2)
C(20)—N(20)—C(21)	111.6 (2)	C(20)—N(20)—C(41)	113.1 (2)
O(31)—C(32)—O(32)	125.1 (3)	O(21)—C(22)—O(22)	124.9 (3)
O(11)—C(12)—O(12)	124.7 (3)	O(41)—C(42)—O(42)	124.8 (3)

(ii) H₂ZnL(H₂O)·H₂O

(a) Zn(1)			
N(10)—Zn(1)—N(20)	82.14 (10)	N(10)—Zn(1)—O(21)	149.89 (8)
N(10)—Zn(1)—O(31)	76.71 (8)	N(10)—Zn(1)—O(41)	97.85 (8)
N(10)—Zn(1)—O(51)	99.16 (11)	N(20)—Zn(1)—O(21)	77.78 (10)
N(20)—Zn(1)—O(31)	94.58 (9)	N(20)—Zn(1)—O(41)	82.38 (9)
N(20)—Zn(1)—O(51)	174.15 (9)	O(21)—Zn(1)—O(31)	82.74 (8)
O(21)—Zn(1)—O(41)	101.42 (8)	O(21)—Zn(1)—O(51)	103.11 (11)
O(31)—Zn(1)—O(41)	174.14 (10)	O(31)—Zn(1)—O(51)	91.27 (10)
O(41)—Zn(1)—O(51)	91.79 (9)		
(b) Zn(1')			
N(10')—Zn(1')—N(20')	80.87 (10)	N(10')—Zn(1')—O(21')	149.72 (8)
N(10')—Zn(1')—O(31')	75.38 (8)	N(10')—Zn(1')—O(41')	96.11 (9)
N(10')—Zn(1')—O(51')	98.55 (12)	N(20')—Zn(1')—O(21')	78.32 (9)
N(20')—Zn(1')—O(31')	94.02 (8)	N(20')—Zn(1')—O(41')	82.72 (9)
N(20')—Zn(1')—O(51')	172.88 (10)	O(21')—Zn(1')—O(31')	84.38 (8)
O(21')—Zn(1')—O(41')	102.75 (10)	O(21')—Zn(1')—O(51')	104.75 (12)
O(31')—Zn(1')—O(41')	171.31 (9)	O(31')—Zn(1')—O(51')	92.69 (9)
O(41')—Zn(1')—O(51')	90.30 (10)		
(c) Chelate rings			
Zn(1')—N(10')—C(10')	106.3 (2)	N(10')—C(10')—C(20')	120.6 (3)
C(10')—C(20')—N(20')	120.8 (3)	C(20')—N(20')—Zn(1')	110.0 (2)
Zn(1')—N(10')—C(31')	105.7 (2)	N(10')—C(31')—C(32')	111.0 (2)
C(31')—C(32')—O(31')	121.8 (2)	C(32')—O(31')—Zn(1')	114.8 (2)
Zn(1')—N(20')—C(21')	104.8 (2)	N(20')—C(21')—C(22')	110.9 (3)
C(21')—C(22')—O(21')	118.2 (3)	C(22')—O(21')—Zn(1')	112.2 (2)
Zn(1')—N(20')—C(41')	104.9 (2)	N(20')—C(41')—C(42')	113.9 (3)
C(41')—C(42')—O(41')	118.1 (2)	C(42')—O(41')—Zn(1')	115.1 (2)
Zn(1')—N(10')—C(10')	106.4 (2)	N(10')—C(10')—C(20')	120.1 (2)
C(10')—C(20')—N(20')	121.1 (3)	C(20')—N(20')—Zn(1')	110.4 (2)
Zn(1')—N(10')—C(31')	103.8 (2)	N(10')—C(31')—C(32')	110.3 (3)
C(31')—C(32')—O(31')	121.9 (3)	C(32')—O(31')—Zn(1')	114.5 (2)
Zn(1')—N(20')—C(21')	104.7 (2)	N(20')—C(21')—C(22')	112.5 (3)
C(21')—C(22')—O(21')	118.4 (3)	C(22')—O(21')—Zn(1')	111.9 (2)
Zn(1')—N(20')—C(41')	104.2 (2)	N(20')—C(41')—C(42')	113.8 (3)
C(41')—C(42')—O(41')	118.2 (3)	C(42')—O(41')—Zn(1')	116.4 (2)
(d) Others			
C(10')—N(10')—C(11')	112.3 (2)	C(10')—N(10')—C(31')	112.8 (2)
C(20')—N(20')—C(21')	111.8 (2)	C(20')—N(20')—C(41')	112.9 (3)
O(11')—C(12')—O(12')	123.6 (3)	O(21')—C(22')—O(22')	126.5 (4)
O(31')—C(32')—O(32')	123.4 (3)	O(41')—C(42')—O(42')	124.4 (3)
C(10')—N(10')—C(11')	111.3 (2)	C(10')—N(10')—C(31')	112.6 (2)
C(20')—N(20')—C(21')	110.4 (2)	C(20')—N(20')—C(41')	114.0 (2)
O(11')—C(12')—O(12')	122.3 (4)	O(21')—C(22')—O(22')	126.7 (3)
O(31')—C(32')—O(32')	124.2 (3)	O(41')—C(42')—O(42')	124.1 (3)

bonded to O(12) of the dissociated carboxyl group and O(32) in H₂ZnL(H₂O)·H₂O. In both crystals the distance between a carboxyl carbon C(*i*2) and O(*i*1) bound to Zn is longer than or nearly equal to that between C(*i*2) and a free O(*i*2). The only exception is found for O(31)—C(32)—O(32) in the diprotonated complex. Thus the shorter C(32)—O(31) bond has a double-bond character and the longer C(32)—O(32) bond may result from the protonation of O(32).

As is evident from Fig. 1 and Table 3, the polyhedron is twisted towards a trigonal prismatic configuration, which has been found for Co^{II}-phdta (McCandlish *et al.*, 1978). On the other hand the protonated species retrieves the octahedral geometry to a considerable extent by dissociation of a carboxyl group from the central metal ion. Comparison of Zn—N bond lengths with those of Zn—edta (Pozhidaev, Polynova, Porai-Koshits & Neronova, 1973; Solans, Font-Altaba, Oliva & Herrera, 1983) shows that the mean values [2.188 Å for K₂ZnL·3H₂O; 2.194 Å for H₂ZnL(H₂O)·H₂O] of the Zn—phdta complexes are considerably longer than

Fig. 2. Packing diagrams of (a) K₂[Zn(phdta)]·3H₂O projected along b, and (b) [Zn(H₂phdta)(H₂O)]·H₂O projected along c.

the corresponding values (2.114 Å for the former; 2.154 Å for the latter) of the edta complexes. This may result from the lowered electron density on the N atoms in the phdta complexes (Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985) as well as a stereochemical requirement imposed by the planar N—C—C—N linkage in the *o*-phenylenediaminetetraacetate anion. Although no general rule is found for Zn—O bonds, the shortest one in the three zinc complex molecules is the Zn—O(H₂O) bond of the protonated phdta complex. The diamine-containing chelate ring is practically planar judging from the sum of the interior angles, which is nearly equal to 540° [539.9° for K₂ZnL·3H₂O; 539.9 and 538.9° for H₂ZnL(H₂O)·H₂O]. This is not the case, however, for any of the glycinate rings in both phdta complexes [520.9–536.8° for K₂ZnL·3H₂O; 523.8–535.4° for H₂ZnL(H₂O)·H₂O], while one of the four rings is almost planar in the edta complexes (539.5°).

Differing from the heptacoordinate structure of hydrated Mn^{II}-phdta (Nakasuka, Azuma, Katayama, Honda, Tanaka & Tanaka, 1985) or monoaquamanganese(II)-edta (Richards, Pedersen, Silverton & Hoard, 1964), zinc(II) and cobalt(II) complexes of phdta are hexacoordinate. These metal ions are relatively smaller than the manganese(II) ion, and the ligand anion manages to encircle the former metal ions. However, it is no longer possible for the ligand to encircle the larger manganese(II) ion completely, and a water molecule must coordinate to the central metal ion to give rise to the heptacoordinate structure for the manganese(II) complexes.

Packing diagrams are given in Fig. 2.

We wish to thank Dr C. Katayama and Miss M. Honda for their helpful discussions. This work was financially supported in part by a Grant-in-Aid for Scientific Research No. 59430010 from the Ministry of Education, Science and Culture.

References

- FURUSAKI, A. (1979). *Acta Cryst.* A35, 220–224.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 95. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KATAYAMA, C., SAKABE, N. & SAKABE, K. (1972). *Acta Cryst.* A28, S207.
 MCCANDLISH, E. F. K., MICHAEL, T. K., NEAL, J. A., LINGAFELTER, E. C. & ROSE, N. J. (1978). *Inorg. Chem.* 17, 1383–1394.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 MOTHERWELL, W. D. S. (1978). *PLUTO78*. Program for drawing crystal and molecular structures. Univ. of Cambridge, England.
 NAKASUKA, N., AZUMA, S., KATAYAMA, C., HONDA, M., TANAKA, J. & TANAKA, M. (1985). *Acta Cryst.* C41, 1176–1179.
 NAKASUKA, N., KUNIMATSU, M., MATSUMURA, K. & TANAKA, M. (1985). *Inorg. Chem.* 24, 10–15.
 POZHIDAIEV, A. I., POLYNOVA, T. N., PORAI-KOSHITS, M. A. & NERONOVA, N. N. (1973). *Zh. Strukt. Khim.* 14, 570–571.
 RICHARDS, S., PEDERSEN, B., SILVERTON, J. V. & HOARD, J. L. (1964). *Inorg. Chem.* 3, 27–33.
 SOLANS, X., FONT-ALTABA, M., OLIVA, J. & HERRERA, J. (1983). *Acta Cryst.* C39, 435–438.

Acta Cryst. (1986). C42, 677–679

Acetyldicarbonyl(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)- [*o*-phenylenebis(dimethylarsine)]iron(II) Tetrafluoroborate

BY M. J. NEWLANDS* AND M. F. MACKAY

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

(Received 13 August 1984; accepted 16 January 1986)

Abstract. [Fe(C₂H₃O)(CO)₂(C₆H₁₁O₃P)(C₁₀H₁₆As₂)]·BF₄, *M_r* = 689.9, monoclinic, *P*2₁/*n*, *a* = 16.824 (2), *b* = 9.384 (1), *c* = 17.189 (2) Å, β = 93.50 (3)°, *V* = 2708.7 (9) Å³, *D_m* = 1.67 (floatation), *D_x* = 1.69 Mg m⁻³, *Z* = 4, λ(Cu Kα) = 1.5418 Å, μ =

8.00 mm⁻¹, *F*(000) = 1384, *T* = 289 K. *R* = 0.087 for 2538 observed terms. In the complex cation, the geometry about Fe is distorted octahedral with a carbonyl *trans* to each As atom and acetyl group *trans* to P. When *trans* to As the Fe—C bond has a mean length 1.76 (2) Å, and when *trans* to P it is 2.00 (2) Å. The Fe—As and Fe—P bonds have lengths 2.366 (2) (mean) and 2.217 (4) Å respectively. The BF₄⁻ anion is disordered.

* On sabbatical leave from Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7.