Structural Studies in Metal–Purpurate Complexes. Part 1. Crystal Structures of Potassium Purpurate Trihydrate and Ammonium Purpurate Monohydrate (Murexide)

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The crystal structures of the title compounds, $[K][L]\cdot 3H_2O$(1) and $[NH_4][L]\cdot H_2O$(2) (L = purpurate, $[C_8H_4N_5O_6]^-$) have been determined at 295 K by *X*-ray diffraction and refined by full-matrix least squares to *R* 0.059 (517 ' observed ' reflections) and 0.080 (874 ' observed ' reflections) respectively. Crystals of both are orthorhombic. For (1) (space group *Ibca*), *a* = 21.75(1), *b* = 16.512(3), *c* = 7.4304(7) Å, *Z* = 8; for (2) (space group *Pbnn*), *a* = 4.5688(8), *b* = 15.309(5), *c* = 17.011(4) Å, *Z* = 4. In both structures, the anion has crystallographic symmetry 2, the angles at the central nitrogen being 126.3(7) (1) and 125.8(4)° (2). The two approximately planar barbiturate rings of each anion are not coplanar with each other, the interaction between neighbouring carbonyl groups causing torsion about the central nitrogen–carbon bonds. In both structures anion–cation interaction and hydrogen bonding is extensive.

THE purpurate anion, $[C_8H_4N_5O_6]^-$(= L), has been widely used in complexometric studies as the ammonium salt, $[NH_4][L]$, murexide, an early synthetic dyestuff.† There is a considerable literature on the subject, almost entirely concerned with solutions. The stoicheiometries of the complexes formed in solution, usually established by Job's method or a similar procedure, are almost exclusively 1 : 1 metal–ligand derivatives. A recent structure determination [1] of the lithium salt $[Li][L]\cdot 2H_2O$ shows that in that derivative the ligand adopts a bent non-planar disposition, the approximately planar ring systems being non-coplanar with each other by virtue of steric hindrance between adjacent carbonyl groups brought into proximity by the trigonal angle at the central nitrogen. In this configuration the ligand effectively co-ordinates the lithium in a tridentate manner as shown in Figure 1. Changes in solution spectrum as a function of cation size suggested that complexation of the above type persisted, but with changes in the torsion about the central nitrogen.[2] A preliminary crystallographic study carried out earlier on the potassium salt [3] had shown that the symmetry constraints of the space group required the ligand to have either *i* or C_2 symmetry, but the matter was not conclusively resolved.

In view of the paucity of structural information about the purpurate species and its complexes, the present study was undertaken to isolate metal derivatives as solids and to characterize a selection of them structurally, if possible ascertaining both the geometry of the free purpurate ion and the manner in which it varies throughout its metal salts and complexes, and determining the

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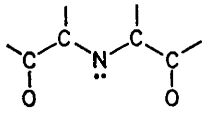
† The purpurate anion has also been referred to in the literature as 5,5′-nitrilodibarbiturate, and purpuric acid as 5-[hexahydro-2,4,6-trioxo-5-pyrimidinylimino]pyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione.

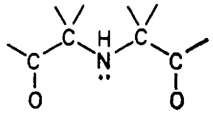
[1] H. B. Bürgi, S. Djurić, M. Dobler, and J. D. Dunitz, *Helv. Chim. Acta*, 1972, **55**, 1771.

[2] R. Winkler, *Structure and Bonding*, 1972, **10**, 1.

[3] A. B. Blake, *Nature*, 1966, **212**, 67.

co-ordination types produced. The results of this study are described in the present and subsequent papers. The only other related systems previously studied structurally based on a tridentate ligand skeleton of the present type (A) are complexes of the pyridine-2,6-dicarboxylate (dipicolinate) ion with a variety of metal ions.[4] Complexes of the iminodiacetate ion have also been studied (B) [5] with a tetrahedral central nitrogen atom. Not all the complexes studied of this ligand contain it in its tridentate form.


(A)


(B)

EXPERIMENTAL

Crystals of all the purpurates studied by us were obtained from aqueous solutions of murexide and a suitable salt, usually the nitrate, of the cation concerned. They are, typically, small, being difficult to grow larger than the lower limit of size suitable for X-ray work. Their structures are strongly hydrogen-bonded, properties which manifest themselves as rather weak but extensive data sets with narrow reflection widths, which lead to rather high residuals but often good accuracy in the structural parameters. Crystallographically, a number of experimental and computational features are common to all structural studies reported in this series. A Syntex $P\bar{1}$ four-circle diffractometer was used for cell determination and data collection throughout; cell dimensions have been obtained from a least-squares fit of the angular parameters of *ca.* 15 reflections with 2θ *ca.* 25° centred in the counter aperture, monochromatic Mo-$K_{\bar{\alpha}}$ radiation ($\lambda = 0.710\,69$ Å) being used for all cell determinations and data collection except for the potassium salt for which Ni-filtered Cu-$K_{\bar{\alpha}}$ radiation ($\lambda = 1.5418$ Å) was employed. Unique data sets have been measured within a 2θ range specified for each derivative, a conventional 2θ—θ scan being used; data sets for structure solution and refinement use ' observed ' reflections only, the criterion being $I > 2\sigma(I)$. The temperature in all cases was 295(1) K. For refinement purposes, neutral atom scattering factors were employed throughout, K^+ excepted, metal atoms being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[6,7] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$. Refinement was terminated in all cases when parameter shifts fell below 0.2σ; refinement modes were full-matrix least squares where the size of the asymmetric unit permitted, otherwise block-diagonal 9×9, or larger (usually) in order to approximate a full-matrix procedure by refining all ligand parameters and/or the parameters of the metal and its environment jointly. The function minimized was $\Sigma w||F_o| - |F_c||^2$; final residuals quoted are $R = \Sigma||F_o| - |F_c||/\Sigma|F_c|$ and $R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$. The weighting scheme used throughout was of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$, the variable parameter n being optimized for each structure. Least-squares planes are referred to the orthogonal right-handed (Å) frame (X,Y,Z) defined by X parallel to a, Z in the ac plane. Computation throughout used a local adaptation of the 'X-Ray '72'

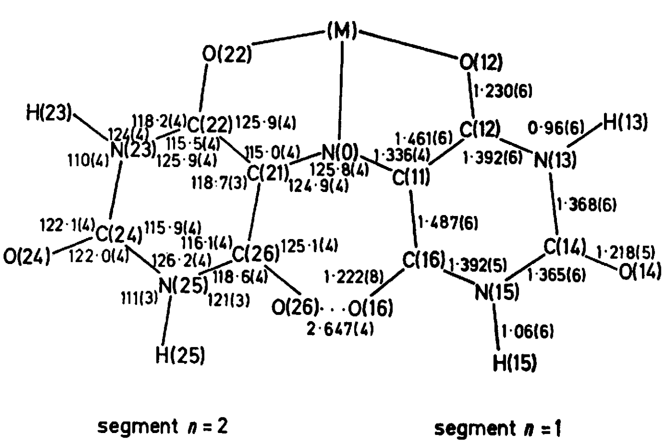


FIGURE 1 Diagram of the purpurate species showing the relative disposition of the two barbiturate rings and the mode of co-ordination as a tridentate ligand about a central metal atom. The numbering scheme adopted in this and subsequent papers is shown; in the present cases, segment 2 of the ligand is not crystallographically independent, being derived from segment 1 by a 2-axis. The geometry given is that of (2), the more accurate of the two present structures

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[4] G. Strahs and R. E. Dickerson, *Acta Cryst.*, 1968, **B24**, 571 ($\mathrm{Ca^{II}}$); K. J. Palmer, R. Y. Wong, and J. C. Lewis, *Acta Cryst.*, 1972, **B28**, 223 ($\mathrm{Sr^{II}}$); L. Baracco, G. Bombieri, S. Degetto, E. Forsellini, R. Graziani, and G. Marangoni, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 1045; A. Immirzi, G. Bombieri, S. Degetto, and F. Marangoni, *Acta Cryst.*, 1975, **B31**, 1023; G. Marangoni, S. Degetto, R. Graziani, G. Bombieri, and E. Forsellini, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1787 ($\mathrm{U^{VI}O_2}$, $\mathrm{U^{IV}}$); B. H. Bersted, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 1968, **7**, 1557; R. E. Drew and F. W. B. Einstein, *Inorg. Chem.*, 1973, **12**, 829 ($\mathrm{V^{IV}O}$); J. Albertsson, *Acta Chem. Scand.*, 1970, **24**, 1213; 1972, **26**, 985, 1005 ($\mathrm{Yb^{III}}$); J. Albertsson, *Acta Chem. Scand.*, 1972, **26**, 1023 ($\mathrm{Nd^{III}}$); D. Schwarzenbach, *Inorg. Chem.*, 1970, **9**, 2391; *Helv. Chim. Acta*, 1972, **55**, 2990; H. Manohar and D. Schwarzenbach, *Helv. Chim. Acta*, 1974, **57**, 1086 ($\mathrm{Ti^{IV}}$); J. A. Thich, C. C. Ou, D. Powers, B. Vasiliou, D. Mastropaolo, J. A. Potenza, and H. J. Schugar, *J. Amer. Chem. Soc.*, 1976, **98**, 1425 ($\mathrm{Fe^{III}}$); H. Gaw, W. R. Robinson, and R. A. Walton, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 695; A. C. Villa, C. Guastini, A. Musatti, and M. Nardelli, *Gazzetta*, 1972, **102**, 226; P. Quaglieri, H. Loiseleur, and G. Thomas, *Acta Cryst.*, 1972, **B28**, 2583 ($\mathrm{Ni^{II}}$); R. V. Chastain, *Diss. Abs.*, 1966, **27**, 124B, and Ph.D. Thesis, University of Washington (University Microfilms, Ann Arbor, Michigan); M. B. Cingi, A. C. Villa, C. Guastini, and M. Nardelli, *Gazzetta*, 1971, **101**, 825; 1972, **102**, 1026; C. Sarchet and H. Loiseleur, *Acta Cryst.*, 1973, **B29**, 1345 ($\mathrm{Cu^{II}}$); M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.* (*A*), 1970, 1045 ($\mathrm{Ag^{II}}$).

[5] A. B. Corradi, C. G. Palmieri, M. Nardelli, M. A. Pellinghelli, and M. E. V. Tani, *J.C.S. Dalton*, 1973, 655 ($\mathrm{Co^{III}}$); J. Albertsson and Å. Oskarsson, *Acta Chem. Scand.*, 1968, **22**, 1700; Å. Oskarsson, *Acta Chem. Scand.*, 1971, **25**, 1206 ($\mathrm{Nd^{III}}$); J. Albertsson and Å. Oskarsson, *Acta Chem. Scand.*, 1974, **A28**, 347 ($\mathrm{Pr^{III}}$); F. G. Kramarenko, T. N. Polynova, M. A. Porai-Koshits, V. P. Chalyi, K. P. Kupriyanova, and L. I. Martynenko, *Zhur. Struct. Khim.*, 1973, **14**, 744; F. G. Kramarenko, T. N. Polynova, M. A. Porai-Koshits, V. P. Chalyi, and N. C. Mitrofanova, *Zhur. Strukt. Khim.*, 1973, **14**, 1113 ($\mathrm{Cu^{II}}$); F. G. Kramarenko, T. N. Polynova, M. A. Porai-Koshits, V. P. Chalyi, and N. D. Mitrofanova, *Zhur. Strukt. Khim.*, 1974, **15**, 161 ($\mathrm{Ni^{II}}$); G. Bombieri, E. Forsellini, G. Tomat, L. Magon, and R. Graziani, *Acta Cryst.*, 1974, **B30**, 2569 ($\mathrm{U^{VI}O_2}$); U. C. Sinkha, F. G. Kramarenko, T. Polynova, M. A. Porai-Koshits, and N. D. Mitrofanova, *Zhur. Strukt. Khim.*, 1975, **16**, 144 ($\mathrm{Zn^{II}}$); A preparative account of the rare-earth derivatives is given in N. M. Prutkova, L. I. Martynenko, A. I. Grigor'ev, and N. D. Mitrofanova, *Russ. J. Inorg. Chem.*, 1966, **11**, 682.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

program system,[8] augmented by ' ORTEP,' [9] implemented on the local CDC 6200 computer. Figure 1 gives the purpurate numbering scheme common to all structures. Final difference maps were computed for all structures and showed no significant features, unless specifically mentioned. Tables of structure amplitudes are deposited as Supplementary Publications to the individual Papers.*

The present paper describes the structure determination of (1), the potassium salt and (2), the ammonium salt, it being surmised in the latter case that the purpurate ligand should display the least interaction of all with the cationic species, $[NH_4]^+$. (In fact, this turned out not to be the case, the purpurate co-ordinating the cation; the clearest example of a ' free ' ligand occurred in a series of derivatives of the type $ML_2{\cdot}nH_2O$ which are actually $[ML(H_2O)_x]$-$[L]{\cdot}6H_2O$ (M = Fe, Co, Zn, or Mn) reported in a subsequent paper[10]).

Crystallographic Data and Procedure.—Compound (1): $C_8H_{10}KN_5O_9$, $M = 359.3$, Orthorhombic, space group *Ibca* (D_{2h}^{27}, No. 73), $a = 21.75(1)$; $b = 16.512(3)$, $c = 7.4304(7)$ Å, $U = 2\,669(1)$ Å^3, $D_m = 1.76(2)$ g cm^{-1}, $Z = 8$, $D_c = 1.79$ g cm^{-3}, $F(000) = 1\,472$, crystal size 0.08 × 0.08 × 0.12 mm (prism), μ(Cu-K_α) = 37.8 cm^{-1} (no absorption correction applied), data range $2\theta < 100°$ yielding 685 independent reflections (517 ' observed '), final $R = 0.059$, $R' = 0.066$ ($n = 6$).

TABLE 1

Atomic fractional cell co-ordinates [(x,y,z); H, × 10^3; others, × 10^4] and thermal parameters (U_{ij}, × 10^3 Å^2) with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(1) (The potassium salt)									
K*	2 500(—)	2 012(1)	0 000(—)	47(2)	24(1)	63(2)	0(—)	3(2)	0(—)
The purpurate anion									
N(0)*	2 500(—)	5 201(5)	0 000(—)	30(6)	27(5)	43(6)	0(—)	8(6)	0(—)
C(11)	3 045(3)	4 836(4)	0 134(11)	16(4)	30(5)	52(6)	3(4)	−2(5)	4(5)
C(12)	3 565(3)	5 371(5)	−0 278(12)	28(5)	29(5)	59(6)	−5(4)	10(5)	−6(5)
O(12)	3 525(2)	6 055(3)	−0 865(9)	25(3)	20(3)	87(5)	−4(3)	3(3)	14(2)
N(13)	4 147(2)	5 032(4)	−0 025(10)	15(3)	21(4)	68(5)	1(3)	7(4)	7(4)
H(13)	448(4)	537(6)	−045(14)	100(—)					
C(14)	4 264(4)	4 299(5)	0 764(12)	23(5)	24(5)	56(6)	3(5)	−5(4)	−7(4)
O(14)	4 795(2)	4 063(3)	1 021(8)	15(4)	30(3)	88(5)	4(2)	1(3)	4(3)
N(15)	3 771(3)	3 854(4)	1 241(10)	15(4)	25(4)	61(3)	−2(3)	−2(4)	6(4)
H(15)	382(4)	342(6)	199(14)	100(—)					
C(16)	3 144(4)	4 052(4)	0 973(11)	26(5)	20(5)	46(5)	0(4)	4(5)	−1(4)
O(16)	2 755(2)	3 597(3)	1 583(7)	23(3)	24(3)	52(4)	−4(3)	6(3)	5(3)
The water molecules									
O(1)	3 834(4)	7 617(4)	1 974(10)	97(6)	32(4)	84(6)	1(4)	36(5)	4(4)
H(1α)	403(5)	791(6)	284(16)	100(—)					
H(1β)	421(5)	759(7)	140(15)	100(—)					
O(2)*	0 000(—)	2 500(—)	0 251(14)	67(6)	44(5)	75(8)	−9(5)	0(—)	0(—)
H(2α) *	000(—)	2 500(—)	214(—)	100(—)					
H(2β)	004(11)	298(11)	−043(30)	100(—)	(population 0.5)				
(2) (The ammonium salt)									
The ammonium cation									
N *	2 500(—)	−2 345(4)	2 500(—)	41(4)	28(3)	49(4)	0(—)	—2(3)	0(—)
H(α)	109(14)	−273(4)	216(3)	100(—)					
H(β)	145(15)	−198(4)	280(3)	100(—)					
The purpurate anion									
N(0) *	2 500(—)	−0 368(3)	2 500(—)	27(3)	23(3)	23(3)		1(2)	
C(11)	3 902(9)	0 029(3)	1 911(2)	21(2)	25(2)	19(2)	2(2)	3(2)	−2(2)
C(12)	5 859(9)	−0 532(3)	1 457(2)	21(2)	42(3)	23(2)	1(2)	3(2)	−12(2)
O(12)	6 340(8)	−1 310(2)	1 583(2)	48(2)	29(2)	43(2)	8(2)	11(2)	−4(2)
N(13)	7 398(9)	−0 125(2)	0 853(2)	25(2)	37(2)	26(2)	−2(2)	12(2)	−6(2)
H(13)	886(14)	−041(4)	054(3)	100(—)					
C(14)	6 929(10)	0 705(3)	0 581(2)	26(3)	47(3)	18(2)	−2(3)	4(2)	−4(2)
O(14)	8 276(8)	1 003(2)	0 025(2)	36(2)	65(2)	29(2)	0(2)	14(2)	9(2)
N(15)	4 792(9)	1 168(3)	0 957(2)	32(2)	39(2)	22(2)	0(2)	8(2)	9(2)
H(15)	414(14)	172(4)	062(3)	100(—)					
C(16)	3 163(10)	0 888(3)	1 600(2)	23(2)	28(2)	20(2)	−5(2)	1(2)	−3(2)
O(16)	1 104(7)	1 336(2)	1 818(2)	35(2)	34(2)	30(2)	8(2)	10(2)	3(1)
The water molecule (hydrogen atoms not located) (population 0.5)									
O(1)	2 605(17)	2 574(7)	4 788(3)	67(4)	35(4)	31(5)	−10(5)	10(3)	−22(5)

* Special position.

The structure was solved by the heavy-atom method and refined by full-matrix least squares, non-hydrogen atomic thermal parameters being refined anisotropically. Hydrogen-atom positional parameters only were refined, U(iso-

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* The Supplementary Publication for the present paper is No. SUP 21987 (11 pp, 1 microfiche); for details see *J.C.S. Dalton*, 1976, Index issue.

[8] ' The *X*-RAY System,' version of June 1972, Technical Report TR 192 of the Computer Science Centre, University of Maryland, U.S.A.

[9] C. K. Johnson, ' ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, ' Technical report ORNL–3794, Oak Ridge National Laboratory, Tennessee, U.S.A.

[10] M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, Part 3, *J.C.S. Dalton*, 1977, 1350.

tropic) being constrained to 0.10 Å^2. The hydrogen atoms about O(2) in one of the lattice water molecules appear to be disordered, since O(2) has site symmetry 2, and a region of electron density was located in a difference map on the 2-axis at a distance somewhat greater than a normal O–H distance. The magnitude of this residual density suggested it to be a fully occupied hydrogen site and it was refined as such [H(2α)]; a second lesser pair of symmetry related sites were refined as H(2β) with an occupancy of 0.5. The possibility that ' H(2α) ' is a small disordered component of O(2) was considered but not pursued in view of the limitations of the data.

Compound (2). $C_8H_{10}N_6O_7$, $M = 302.2$, Orthorhombic, space group *Pbnn* (variant of D_{2h}^6, No. 52) (x,y,z; $x, \frac{1}{2} - y, \bar{z}$; $\frac{1}{2} - x, y, \frac{1}{2} - z$; $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; together with inversion images), $a = 4.5688(8)$, $b = 15.309(5)$, $c = 17.011(4)$ Å, $U = 1\,189.6(8)$ Å^3, $D_m = 1.72(2)$ g cm^{-3}, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 624$, crystal size $0.08 \times 0.08 \times 0.11$ mm (prism), μ(Mo-K_α) = 1.00 cm^{-1} (no absorption correction applied), data range $2\theta < 60°$ yielding 1 758 independent reflections (874 ' observed '), final $R = 0.080$, $R' = 0.070$ ($n = 2$).

The structure was solved by direct methods and refined by full-matrix least squares, non-hydrogen-atom thermal parameters being refined anisotropically. Hydrogen-atom positional parameters only were refined, U(isotropic) being constrained to 0.10 Å^2. The lattice water molecule is disordered about a two-fold axis and the oxygen O(1) was refined with a population of 0.5, no associated hydrogen atoms being located. The possibility that this ' disorder ' may have been an artefact of an incorrect choice of space group was considered but not pursued, since the structure showed no anomalies in other respects and it seemed unlikely that the problem would be successfully resolved in view of the rather weak data set.

Atomic fractional cell co-ordinates and thermal parameters for compounds (1) and (2) are given in Table 1.

DISCUSSION

Anion Geometry.—In both the structures under consideration, the crystal lattice comprises potassium or ammonium cations, purpurate anions, and lattice water molecules. The purpurate species in both structures have crystallographically imposed symmetry 2 rather than the *i* symmetry suggested as an alternative in the previous study of the potassium salt [3] on the basis of the space-group requirement $Z = 8$. In this they resemble the anion of the lithium salt [1] in which a similar non-crystallographically imposed symmetry is found, and there is no suggestion in any of the further studies carried out by us that the anion symmetry is *i* (with a linear central nitrogen) rather than 2 (with a trigonal central nitrogen). The symmetry requirement of 2 in the present structures implies equivalence of the two barbiturate rings; again there is no evidence from our latter studies to suggest that the purpurate anion geometry differs from 2 symmetry other than trivially in the absence of a crystallographically imposed 2-axis. The present structure determinations were carried out in the hope of defining the unperturbed purpurate geometry in an unco-ordinated anion; in the present structures, the anion interacts strongly with the cation and it is likely that a better example of unperturbed anion geometry is to be found in the iron derivative $[FeL(H_2O)_3][L]\cdot6H_2O$ reported subsequently; [10] the latter structure has the additional virtue of being more accurate. The difference in geometry is only trivial, however, and discussion of the geometry of the unperturbed anion will be continued in terms of the present structures.

Consideration of the anion geometries (Table 2) suggests that, in the mean anion structure shown in Figure 1, considerable π-electron delocalization is found throughout the ring systems. (Usual single- and double-bond lengths are: C–C, 1.54; C=C, 1.33; C–N, 1.47; C=N, 1.30; C–O, 1.43; C=O, 1.21 Å, ref. 11.) This may be rationalized in terms of contributions by a number of neutral and anionic resonance forms of the type shown in Figure 2. It is apparent, however, that delocalization is only partial (the CO groups, for example, retain almost total double-bond character), and is not fully effective in inducing planarity either within the barbiturate ring or about the central trigonal nitrogen N(0). Atom deviations from the plane defined by the ring atoms are indicative of a small nonplanar ' boat ' distortion; this is particularly evident when the peripheral oxygen atoms are considered. One source of the ' boat ' distortion appears to lie in the interaction between the pair of oxygens O(n6) of the same purpurate, which in the case of a planar molecule would lie at a distance considerably smaller than the van der Waals sum. The overall purpurate disposition is one in which the pair of barbiturate ring ' planes ' are not coplanar with the central N(0) but are twisted about the C(11)–N(0) bonds to an extent which, while still permitting a considerable π-electron delocalization through the central nitrogen, reduces the O(16) · · · O(26) interaction so that the latter lie separated by *ca.* 2.60 Å; this latter distance is appreciably less than the commonly accepted value for an O · · · O van der Waals sum of

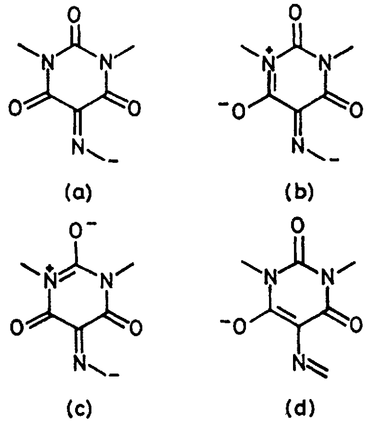

FIGURE 2 This diagram shows the nature of the most probable neutral [(a)—(c)] and anionic (d) resonance forms contributing to the structure of the purpurate species. [The list is not exhaustive. For example, forms are given for the left-hand side of the ring only. Likewise, combinations of various forms, *e.g.* (c) and (d), are possible]

[11] ' Tables of Interatomic Distances and Configuration in Molecules and Ions,' Chemical Society Special Publication, No. 18.

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses

(*a*) The purpurate geometry [structures (1) and (2)]. Attention is drawn in this and subsequent papers to the disposition of entries in parallel columns to facilitate the comparison of the geometries of the two halves of the barbiturate ring demarcated by the N(0), C(11), C(14), O(14) ring ' axis '

Compound	(1)	(2)
N(0)–C(11)	1.336(8)	1.336(4)
C(11)–C(12)	1.465(10)	1.461(6)
C(12)–O(12)	1.214(10)	1.230(6)
C(12)–N(13)	1.398(9)	1.392(6)
N(13)–H(13)	0.96(9)	0.96(6)
N(13)–C(14)	1.368(11)	1.368(6)
C(14)–O(14)	1.234(9)	1.218(5)
C(11)–N(0)–C(21)	126.3(7)	125.8(4)
N(0)–C(11)–C(12)	113.4(7)	115.0(4)
C(11)–C(12)–O(12)	125.4(7)	125.9(4)
O(12)–C(12)–N(13)	119.1(7)	118.2(4)
C(11)–C(12)–N(13)	115.4(7)	115.8(4)
C(12)–N(13)–H(13)	113(6)	124(4)
H(12)–N(13)–C(14)	121(6)	110(4)
C(12)–N(13)–C(14)	125.4(6)	125.9(4)
N(13)–C(14)–O(14)	121.3(7)	122.1(4)
N(13)–C(14)–N(15)	116.6(7)	115.9(4)
C(12)–C(11)–C(16)	120.9(6)	118.7(3)
C(11)–C(16)	1.453(10)	1.457(6)
C(16)–O(16)	0.219(9)	1.222(5)
C(16)–N(15)	1.415(10)	1.392(5)
N(15)–H(15)	0.92(10)	1.06(6)
N(15)–C(14)	1.348(10)	1.365(6)
O(16) · · · O(26)	2.602(7)	2.647(4)
[O(26)≡O(16$^{\text{I}}$)]		
N(0)–C(11)–C(16)	124.4(7)	124.9(4)
C(11)–C(16)–O(16)	127.3(7)	125.1(4)
O(16)–C(16)–N(15)	118.3(7)	118.6(4)
C(11)–C(16)–N(15)	114.0(6)	116.1(4)
C(16)–N(15)–H(15)	113(6)	121(3)
H(15)–N(15)–C(14)	119(6)	111(3)
C(16)–N(15)–C(14)	127.2(7)	126.2(4)
N(15)–C(14)–O(14)	122.2(7)	122.0(4)

(*b*) Compound (1), remaining geometry

(*i*) The water molecules

O(1)–H(1α)	0.91(11)	O(2)–H(2α)	1.40(–)
O(1)–H(1β)	0.93(10)	O(2)–H(2β)	0.95(19)
H(1α)–O(1)–H(1β)	86(9)	H(2α)–O(2)–H(2β)	122(13)
		H(2β)–O(2)–H(2β$^{\text{II}}$)	116(18)

(*ii*) Hydrogen-bonded interactions (O · · · H, <2.5 Å); the angle subtended at the hydrogen atom is given in parentheses

H(13) · · · O(14$^{\text{III}}$)	1.89(9)	H(15) · · · O(1$^{\text{IV}}$)	1.88(10)
	[171(9)]		[165(9)]
H(1α) · · · O(12$^{\text{V}}$)	2.26(11)	H(1β) · · · O(2$^{\text{VI}}$)	1.92(10)
	[118(8)]		[179(10)]
H(2α) · · · O(2$^{\text{VII}}$)	2.31(1)		
	[180(–)]		

(*iii*) The potassium environment; contacts and angles are listed for K · · · O <3.0 Å. There is an additional longer contact [K · · · O(1$^{\text{VIII}}$), 3.402(8) Å] shown in Figure 3 for which the associated angles are not tabulated

K · · · O(16,16$^{\text{I}}$)	2.922(5)
K · · · O(12$^{\text{VIII,XI}}$)	2.807(6)
O(16) · · · K · · · O(16$^{\text{IX}}$)	89.7(1)
O(16) · · · K · · · O(12$^{\text{VIII}}$)	138.4(2)
O(16$^{\text{IX}}$) · · · K · · · O($^{\text{VIII}}$)	81.2(2)
O(16$^{\text{IX}}$) · · · K · · · O(16$^{\text{X}}$)	137.6(2)
O(12$^{\text{VIII}}$) · · · K · · · O(12$^{\text{XI}}$)	111.4(2)
K · · · O(16$^{\text{IX,X}}$)–C(16$^{\text{IX,X}}$)	134.4(5)
K · · · O(16$^{\text{IX}}$,16$^{\text{X}}$)	2.787(5)
K · · · N(0$^{\text{VIII}}$)	2.991(8)
O(16) · · · K · · · O(16$^{\text{I}}$)	52.9(1)
O(16) · · · K · · · O(16$^{\text{X}}$)	130.7(2)
O(16) · · · K · · · O(12$^{\text{XI}}$)	105.2(2)
O(16$^{\text{IX}}$) · · · K · · · O(12$^{\text{XI}}$)	75.3(2)
K · · · O(16,16$^{\text{I}}$)–C(16,16$^{\text{I}}$)	122.2(5)
K · · · O(12$^{\text{VIII,XI}}$)–C(12$^{\text{VIII,XI}}$)	119.9(5)

TABLE 2 (*Continued*)

Transformations of the asymmetric unit (x, y, z) are denoted by the following Roman superscripts

I ($\frac{1}{2} - x, y, \bar{z}$)
II ($\bar{x}, \frac{1}{2} - y, z$)
III ($1 - x, 1 - y, \bar{z}$)
IV ($x, 1 - y, \frac{1}{2} - z$)
V ($x, 1\frac{1}{2} - y, \frac{1}{2} + z$)
VI ($\frac{1}{2} - x, \frac{1}{2} + y, z$)
VII ($\bar{x}, y, \frac{1}{2}, + z$)
VIII ($\frac{1}{2} - x, y - \frac{1}{2}, z$)
IX ($\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$)
X ($x, \frac{1}{2} - y, z - \frac{1}{2}$)
XI ($x, y - \frac{1}{2}, \bar{z}$)

(*c*) Compound (2), remaining geometry

(*i*) The water molecule (disordered; no hydrogen atoms located)

O(1) · · · O(1$^{\text{I}}$)	0.76(1)

(*ii*) The ammonium cation

N–H(α)	1.05(6)	N–H(β)	0.89(6)
H(α)–N–H(β)	110(5)	H(α)–N–H(β$^{\text{I}}$)	112(5)
H(α)–N–H(α$^{\text{I}}$)	112(5)	H(β)–N–H(β$^{\text{I}}$)	102(6)

(*iii*) Hydrogen-bonded interactions (O · · · H, <2.5 Å); the angle subtended at the hydrogen atom is given in parentheses

H(13) · · · O(14$^{\text{III}}$)	1.86(6)	H(15) · · · O(1$^{\text{I}}$)	1.68(6)
	[177(5)]		[166(5)]
H(15) · · · O(1$^{\text{IV}}$)	1.96(6)	H(α) · · · O(15$^{\text{V}}$)	1.84(6)
	[161(5)]		[161(5)]
H(β) · · · O(12$^{\text{II}}$)	1.95(6)		
	[171(6)]		

Transformations of the asymmetric unit (x, y, z) are denoted by the following Roman superscripts:

I ($x, \frac{1}{2} - y, \bar{z}$)
II ($\frac{1}{2} - x, y, \frac{1}{2} - z$)
III ($2 - x, \bar{y}, \bar{z}$)
IV ($\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$)
V ($\bar{x}, y - \frac{1}{2}, z$)

$2 \times 1.40 = 2.80$ Å.[12] It is of interest that the degree of torsion about C(21)–N(0)–C(11)–C(12) is not the same as 180 – [C(21)–N(0)–C(11)–C(16)]°,[10] the latter torsion being greater and reflecting the strain due to the O(16) · · · O(26) interaction superimposed on the restoring force of the π bonding. This interaction is also reflected in the angle at the central nitrogen N(0), which (being *ca.* 126°) is enlarged beyond the trigonal angle of 120°. Similarly in the angles about C(11),N(0)–C(11)–C(16) is considerably greater than N(0)–C(11)–C(12); in fact, a much better barbiturate ring plane is obtained if C(11) is eliminated from the calculation. These phenomena persist in the later structures in the series, correlating with a further strain parameter introduced by the variability in the action and geometry of the purpurate as a tridentate ligand about a central metal atom. In respect of the torsion angle C(11)–N(0)–C(11)–C(16), energy-minimization calculations[1] based on the geometry of the lithium derivative and made with a view to explaining the spectral differences observed in the various alkali-metal salts suggested that the torsion should increase as the size of the alkali metal increased and a value of 30.5° was predicted for the potassium salt, in good agreement with the present observation (–30.2°); the model is clearly faulty however, in as much as it predicts K · · · N(0) and K · · · O(12) distances of 2.61 and 2.74 Å, these values being at serious variance with those observed, the metal–nitrogen distance [2.991(8) Å] being *longer* than the metal–

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[12] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, 1960, p. 260.

TABLE 3

Least-squares planes, calculated through the C(n1,n2,n4,-n6),N(n3,n5) skeleton of the barbiturate segment of the purpurate in the form $pX + qY + rZ = s$, where the right-handed orthogonal (Å) frame is defined with X parallel to a,Z in the ac plane. Atom deviations (Å) are in square brackets with values for compounds (2) in parentheses after those for compound (1). The estimated standard deviations of the defining atoms are in Å. The angle between the normals to the two barbiturate planes of each ligand is denoted θ°

Compound	(1)	(2)
10^4p	−0 122	7 082
10^4q	4 165	3 503
10^4r	9 091	6 130
s	3.365	3.197
σ	0.03	0.05
χ^2	73.0	126
θ	49.2	41.0

[C(11) 0.03 (0.07), C(12) −0.05 (−0.07), N(13) 0.03 (0.02), C(14) 0.01 (0.03), N(15) −0.02 (−0.02), C(16) −0.00 (−0.003), N(0) −0.15 (0.02), O(12) −0.12 (−0.20), O(14) 0.11 (−0.04), O(16) −0.11 (−0.23), K^+ 2.05 ($N\{H_4\}^+$ −1.04)]

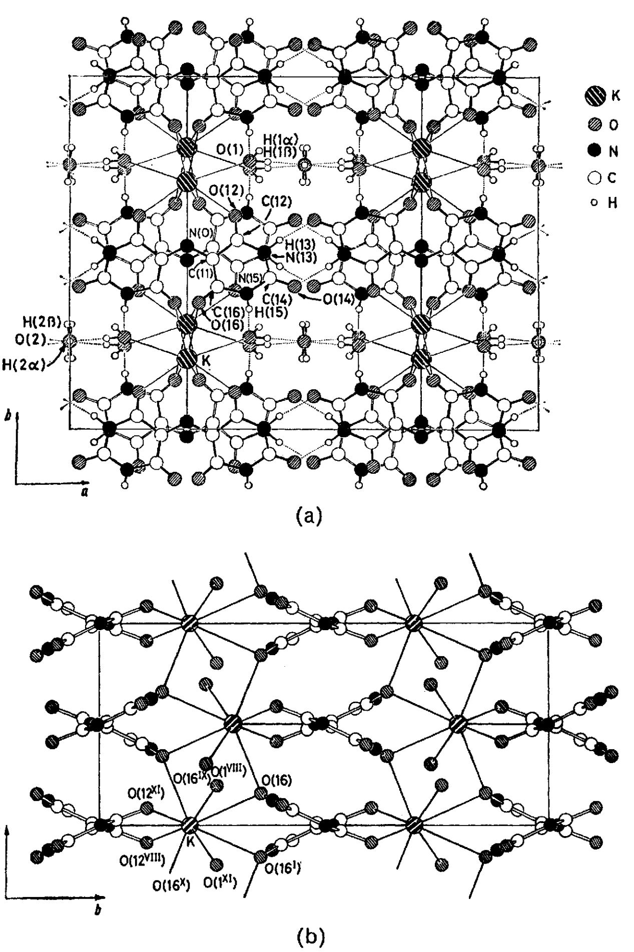

FIGURE 3 (a) Unit-cell contents of (1) projected down c. Bonds within the purpurate species are shown in perspective, bonds of the potassium environment are shown as solid lines and hydrogen bonds as dotted lines. (b) Projection of the potassium ions at x = 0.25 together with their environments, down a, showing the polymeric nature of the potassium–purpurate interactions

oxygen distance [2.807(6) Å] and probably indicative that in these derivatives the metal–nitrogen interaction is rather weak relative to the metal–oxygen. It is possible that this effect may simply be a solid-state phenomenon, since in the potassium derivative there is some interaction between the metal and the close O(16) · · · O(26) pair which may affect the above geometry. However, evidence from later structures with ligands co-ordinated in this manner suggests that the metal–nitrogen distance is normally *ca.* 0.1 Å longer than the metal–oxygen. The K · · · O(n6) interaction appears to be weak; the O(16) · · · O(26) distance is similar to that observed in later structures with no interaction in this position; and the interplanar ligand angle appears to be as expected for the given K · · · O(12) distance. Detailed consideration of individual bond distances and angles within the purpurate is deferred to Part 3 of this series when it becomes possible to make a comparison between co-ordinated and unco-ordinated purpurate species.[10]

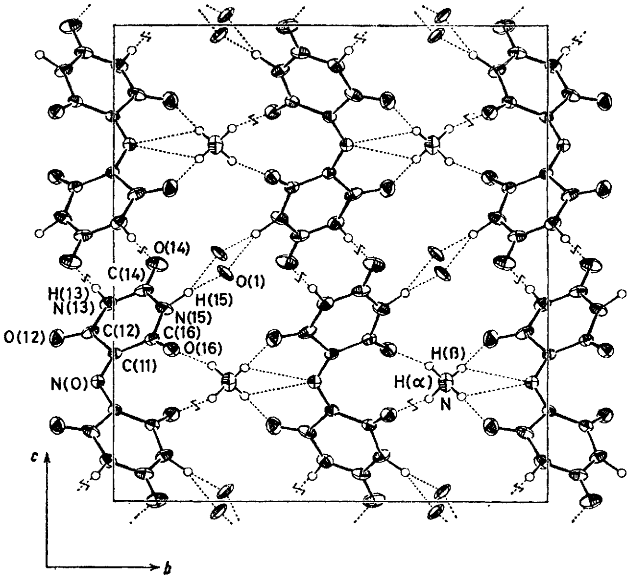

FIGURE 4 Unit-cell contents of (2) projected down a showing 50% thermal ellipsoids, and hydrogen bonding as dotted lines. Hydrogen atoms have an arbitrary radius of 0.1 Å. Breaks in the dotted lines indicate intercellular contacts. The labelled ammonium cation is at $y = 1 + y$

Crystal Packing.—In (2), the purpurate anion lies about a 2 axis ($\frac{1}{4}$,y,$\frac{1}{4}$) passing through N(0); the nitrogen of the ammonium cation also lies on this axis. Cation hydrogens H(α) are ' co-ordinated ' by the tridentate section of the purpurate comprised of N(0) and oxygens O(n2); the cation hydrogens H(β) bridge the oxygens O(n6) of the anions in successive cells along a. The hydrogen bonding is further extended by interaction between purpurate hydrogens H(n3) and the O(n4) of adjacent cells related by the inversion centres along a. The resulting network has interstitial tunnels about (x,$\frac{1}{4}$,$\frac{1}{2}$) and these are occupied by the disordered water molecules, the two oxygen components of which are separated by 0.76 Å and are hydrogen-bonded to purpurate hydrogens H(5). It will thus be appreciated that all purpurate oxygen and hydrogen atoms participate in interactions with neighbouring species in the lattice; this phenomenon is usual among the purpurate derivatives reported in later studies.

The lattice array in (1) is more symmetrical, the purpurate symmetry still being 2 by virtue of the 2-axis at ($\frac{1}{4}$,y,0) passing through N(0). The potassium ion is also coaxial with succeeding purpurate ions distributed along the 2-axes and, as a consequence, we find that if the oxygens O(n2) together with N(0) are defined as the ligand ' head,' H, and the oxygens O(n6) as the ligand ' tail,' T, then there is an array of the type HT $\cdots$ K $\cdots$ HT $\cdots$ K $\cdots$ HT $\cdots$ K along these axes. Oxygens O(n6) in addition, interact with adjacent potassium ions generated by the inversion centres in the plane, x = 0.25, filling two more of the ' co-ordination sites ' about the potassium (Figure 3). The co-ordination about the potassium is thus unusually sparse with only six contacts <3.0 Å, although there is an additional pair of contacts [at 3.402(8) Å] to the water-molecule oxygen atoms O(1). Again we find interstitial tunnels in the lattice about ($\frac{1}{2}$,$\frac{1}{4}$,z) occupied by water molecules possibly disordered in respect of their hydrogen orientations.

[6/054 *Received*, 8*th January*, 1976]