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Crystal Structure of Potassium Dithizonate[†,††]

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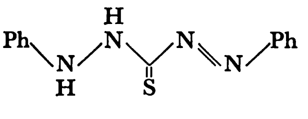
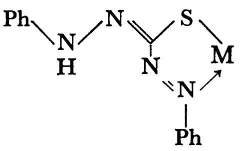
The crystal structure of potassium dithizonate, $K^+[C_6H_5 \cdot NH \cdot N \cdot CS \cdot N:NC_6H_5]^-$, has been determined by single crystal X-ray diffraction methods at 295 K and refined by full matrix least squares to a residual of 0.045 for 1101 independent "observed" reflections. Crystals are orthorhombic, Pbca, a=28.942(9), b=13.247(4), c=7.163(3) Å, Z=8. The structure determination is the first carried out on a salt rather than a complex of the anion. The pseudo-planar anion stacks parallel to the *ab* face of the cell with considerable delocalization evident; as indicated by the above formula, the remaining acidic hydrogen atom is associated with one of the nitrogen atoms.

The well-known analytical reagent dithizone, H_2dz, (A), undergoes both single and double deprotonation, but is best known by way of the numerous, highly-coloured, solvent extractable complexes of the mono-anion, simply referred to usually as the dithizonate anion, Hdz^-.[2)]

For such complexes, a variety of linkage isomers is possible and establishment of the coordination mode has demanded the application of X-ray crystallography. In this way, the bidentate N, S chelating form (B) has been established as "usual," though unidentate coordination through sulfur has also been characterized recently in indium(III) dithizonate,[3)] in which two bidentate (N,S) and one monodentate (S) ligands are found. All known structures have been determined on compounds of metals which show strong coordinating tendencies and no data has been available for dithizonates which might be regarded as essentially ionic. Accordingly, we have prepared the potassium salt of the monoanion, (1), and report its crystal structure hereunder. Because of its ease of preparation and high solubility in many solvents, it is anticipated that this salt should be of some utility in the preparation of other metal dithizonates.



(A)



(B)

Synthesis

Because of the ease of oxidation of the ligand, as a routine precaution, all manipulations were carried out under nitrogen using deoxygenated solvents.

Dithizone (2.5 g) was added to a solution of KOH (0.70 g, ≈5% excess assuming 85% purity) in water (3 mL) and the mixture stirred to give a deep orange solution and then a paste as KHdz precipitated. Ethanol (25 mL) was added to dissolve the paste and the solution filtered to remove a small amount of insoluble material. Addition of ether (≈100 mL) to the point of turbidity and standing at room temperature caused the precipitation of clusters of thin, metallic-brown crystals of KHdz. Crystals suitable for X-ray diffraction were obtained from this material, though it could also be recrystallized from ethanol by the addition of ether.

Crystallography

Crystal Data. $C_{13}H_{11}N_4SK$, M=294.4, Orthorhombic, space group Pbca (D_{2h}^{15}, No. 61), a=28.942 (9), b=13.247 (4), c=7.163 (3) Å, U=2746 (2) Å^3. $D_c(Z=8)$=1.42 g cm^{-3}. $F(000)$=1216. Monochromatic Mo $K\alpha$ radiation, λ=0.71069 Å, μ_{Mo}=5.2 cm^{-1}. Specimen: right prism, 0.20×0.40×0.20 mm. T=295 K.

Structure Determination. A unique data set was measured to $2\theta_{max}$=50° using a Syntex P$\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 2869 independent reflections were obtained, 1101 with $I>3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinement after analytical absorption correction and solution of the structure by direct methods. Anisotropic thermal parameters were refined; $(x, y, z, U_{iso})_H$ were included constrained at idealized geometries (Exception: the NH hydrogen which was located in a difference map and refined in (x, y, z). Residuals at convergence R, R' (on $|F|$) were 0.045, 0.052, reflections weights being $(\sigma^2(F_0)+0.0005(F_0)^2)^{-1}$. Neutral atom complex scattering factors[4)] were used; computation used the X-RAY 76 program system[5)] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Results are presented in the Tables and Figure; atom coordinates for all atoms are given in Table 1, and atom labelling in the Figures.

The lists of structure factors, anisotropic thermal parameters, and non-hydrogen interanion contacts are deposited at the office of the Chemical Society of Japan as Document No. 8504.

Discussion

The result of the structure determination is consistent with the stoichiometry expected for K^+Hdz^-, the

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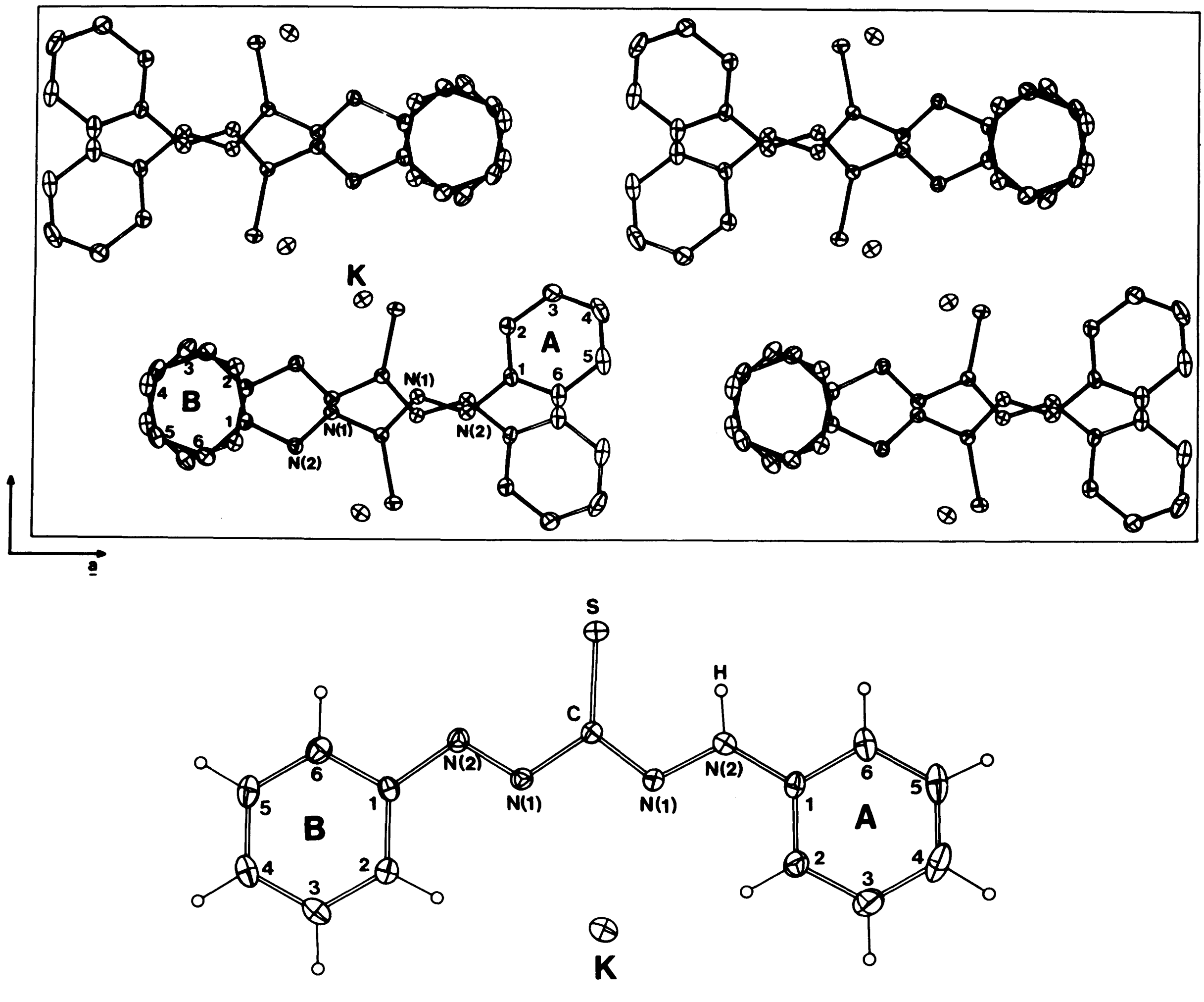
[†] Material deposited with the editor comprises structure factor amplitudes, thermal parameters and inter-anion contacts.

[††] Systematic name: Potassium 1,5-Diphenyl-3-mercapto-formazanate.

TABLE 1. ATOM COORDINATES

Atom	Section A			Section B		
	x	y	z	x	y	z
K	0.28301(5)	0.45023(9)	0.27182(21)			
S	0.31109(5)	0.06809(10)	0.30849(27)			
C	0.3001(2)	0.1944(4)	0.3411(8)			
Ligand						
N(1)	0.3303(1)	0.2681(3)	0.3179(6)	0.2574(1)	0.2368(3)	0.3942(6)
N(2)	0.3729(1)	0.2381(4)	0.2678(8)	0.2267(1)	0.1725(3)	0.4408(6)
H	0.375(2)	0.171(4)	0.251(8)			
C(1)	0.4096(2)	0.3049(4)	0.2592(8)	0.1839(2)	0.2179(4)	0.4974(8)
C(2)	0.4063(2)	0.4010(4)	0.3302(10)	0.1748(2)	0.3211(4)	0.5030(8)
H(2)	0.378(−)	0.424(−)	0.387(−)	0.199(−)	0.367(−)	0.461(−)
C(3)	0.4443(2)	0.4647(5)	0.3206(11)	0.1324(2)	0.3554(5)	0.5618(9)
H(3)	0.443(−)	0.534(−)	0.376(−)	0.128(−)	0.428(−)	0.569(−)
C(4)	0.4849(2)	0.4319(6)	0.2382(11)	0.0986(2)	0.2876(5)	0.6175(9)
H(4)	0.511(−)	0.482(−)	0.232(−)	0.069(−)	0.314(−)	0.657(−)
C(5)	0.4881(2)	0.3356(6)	0.1701(10)	0.1072(2)	0.1871(5)	0.6107(9)
H(5)	0.517(−)	0.318(−)	0.115(−)	0.084(−)	0.139(−)	0.653(−)
C(6)	0.4506(2)	0.2713(5)	0.1801(9)	0.1499(2)	0.1516(5)	0.5521(8)
H(6)	0.453(−)	0.203(−)	0.132(−)	0.156(−)	0.079(−)	0.545(−)

asymmetric unit of the structure comprising one formula unit. The anion is pseudo-planar and approximately parallel to the *ab* face of the cell (Fig. 1(a)); although as discussed below, the central fragment dimensions are indicative of the presence of conjugation, the deviations of the anion from planarity are not confined to the molecular periphery. The plane defined by the $N_2\cdot CS\cdot N_2$ fragment has σ (defining atoms), 0.047 Å; atom deviations δ N(A2,A1)·CS·N(B1, B2) respectively are 0.041, −0.006, −0.022, −0.021, −0.060, 0.068 Å, with the phenyl ring planes ($\sigma(C_6)$, 0.006, 0.004 Å) having dihedral angles of 14.8, 7.3°



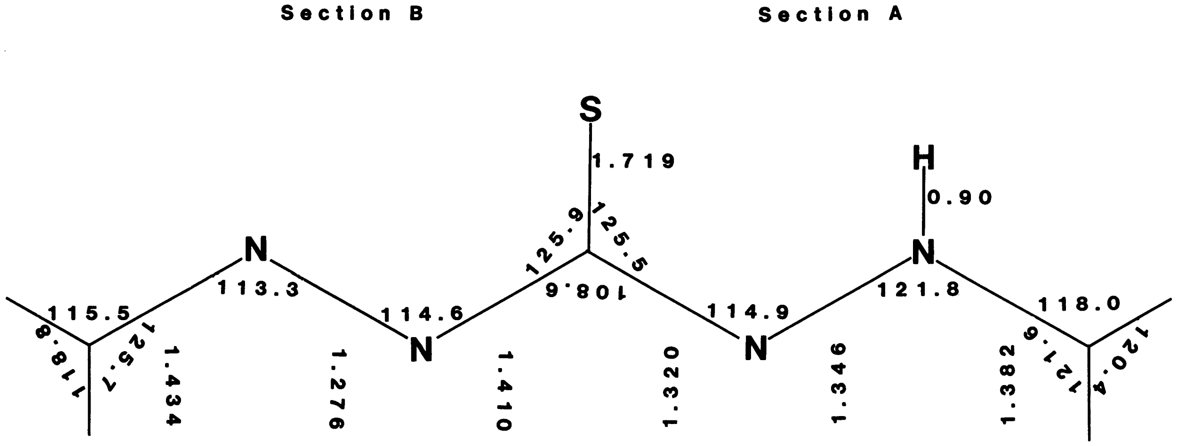


Fig. 1. (a) Unit cell contents, projected down *c*; 20% thermal ellipsoids are shown for the non-hydrogen atoms.

(b) The asymmetric unit, showing the interaction of the anion with the potassium ion and the location of the acidic hydrogen. Non-hydrogen atom numbering is given, and hydrogen atoms are given arbitrary radii of 0.1 Å.

(c) Non-phenyl anion geometry; distances are in Å and angles in degrees.

Table 2. Potassium environment[a)]

	r	N(B1)	S^{i}	N($B2^{i}$)	S^{ii}	N($B2^{ii}$)
N(A1)	2.793(4)	44.3(1)	147.3(1)	142.6(1)	86.4(1)	84.3(1)
N(B1)	3.052(5)		103.0(1)	136.3(1)	105.7(1)	68.3(1)
S^{i}	3.150(2)			55.7(1)	108.7(1)	82.9(1)
N($B2^{i}$)	3.196(5)				116.9(1)	133.0(1)
S^{ii}	3.426(3)					52.2(1)
N($B2^{ii}$)	3.305(5)					

a) *r* is the potassium-ligand atom distance (Å); the other entries are the angles (degrees) subtended by the relevant atoms at the metal.

Transformations of the asymmetric unit: i: (1/2−*x*, 1/2+*y*,*z*), ii: (*x*, 1/2−*y*, *z*−1/2).

respectively to the central plane. For the anion non-hydrogen skeletal plane overall, σ is 0.177 Å, with the potassium ion of the asymmetric unit deviating by 1.274 Å; its deviation from the N_2·CS·N_2 plane is −0.906 Å.

The potassium ion environment is sparse (Table 2); an interesting feature is the disposition within the defined asymmetric unit of the two shortest contacts relative to the anion to N(A1,B1), and, because of anion "planarity," the associated contacts to H(A2,B2) of 2.8_8, 2.9_9 Å. Phenyl ring "B," with the smaller dihedral angle to the N_2·CS·N_2 plane, is reasonably coplanar with the associated NN·CS fragment (deviations, 0.01_8, 0.03_8, 0.077, −0.095, although it is clear that there is a twist about the CS·N_2 linkage), and the potassium ion deviation is −0.428 Å. Phenyl ring "A"'s association with its NN·CS fragment is less equable (deviations 0.006, −0.191, 0.003, 0.442 Å) and indicative of considerable torsion within the string; the potassium deviation is considerable, being −1.703 Å. It may therefore be assumed that the closeness of the association of the potassium with N(A1), in the situation of a planar anion, results in too close an association with H(A2), with the associated strain being relieved by distortion of the ligand plane. Although the other

Table 3. Anion atom geometries
The two values in each entry are for sections A, B

Atom	Parameter
Distances(*l*/Å)	
C-S	1.719(5)
C-N(1)	1.320(7), 1.410(7)
N(1)-N(2)	1.346(6), 1.276(6)
N(2)-H	0.90(5)
N(2)-C(1)	1.382(7), 1.434(7)
C(1)-C(2)	1.374(8), 1.394(8)
C(2)-C(3)	1.388(9), 1.373(9)
C(3)-C(4)	1.385(10), 1.386(9)
C(4)-C(5)	1.369(11), 1.356(10)
C(5)-C(6)	1.383(9), 1.388(9)
C(6)-C(1)	1.389(8), 1.376(8)
Angles(ϕ/°)	
N(1)-C-S	125.5(4), 125.9(4)
N(1)-C-N(1)	108.6(4)
C-N(1)-N(2)	114.9(4), 114.6(4)
N(1)-N(2)-C(1)	121.8(5), 113.3(4)
N(2)-C(1)-C(2)	121.6(5), 125.7(5)
N(2)-C(1)-C(6)	118.0(5), 115.5(5)
C(2)-C(1)-C(6)	120.4(5), 118.8(5)
C(1)-C(2)-C(3)	119.4(6), 120.2(5)
C(2)-C(3)-C(4)	120.2(6), 120.3(6)
C(3)-C(4)-C(5)	120.1(6), 119.8(6)
C(4)-C(5)-C(6)	120.1(6), 120.4(6)
C(5)-C(6)-C(1)	119.7(6), 120.5(6)

TABLE 4. COMPARATIVE DITHIZONE GEOMETRIES

	(1)(A)	(3)(A′)	(3)(A)		(2)	(3)(B)		(3)(B′)	(1)(B)
					Distances(l/Å)				
C–S	1.719(5)	1.761(8)	1.754(8),	1.763(8)	1.71				
C–N	1.410(7)	1.410(9)	1.363(10),	1.374(10)	1.34_5	1.328(9),	1.310(8)	1.305(11)	1.320(7)
N–N(H)	1.276(6)	1.274(10)	1.293(8),	1.290(8)	1.29_5	1.326(9),	1.317(10)	1.324(9)	1.346(6)
N(H)–C(aryl)	1.434(7)	1.437(9)	1.403(10),	1.419(10)	1.38_5	1.410(10),	1.407(9)	1.409(12)	1.382(7)
					Angles(ϕ/°)				
N–C–S	125.9(4)	123.5(6)	125.5(5),	125.5(5)	125	123.6(6),	123.4(6)	123.4(5)	125.5(4)
N–C–N	108.6(4)	112.5(7)	110.7(6),	111.1(6)	110				
C–N–N(H)	114.6(4)	114.8(6)	119.5(6),	117.6(6)	115	117.3(6),	116.9(6)	117.2(7)	114.9(4)
N–N(H)–C(aryl)	113.4(4)	112.9(6)	116.0(6),	114.6(6)	122	117.4(6),	122.5(7)	120.6(8)	121.8(5)

Species compared are: (1)(A) Unprotonated section of the present dithizonate anion. (3)(A′) Unprotonated section of the S-coordinated ligand of indium(III) dithizonate. (3)(A) Coordinated sections of the chelate ligands of indium(III) dithizonate. (2) The mean of both (protonated) sections of the parent dithizone molecule. (3)(B) Uncoordinated sections of the chelate ligands of indium(III) dithizonate. (3)(B′) Protonated section of the S-coordinated ligand of indium(III) dithizonate. (1)(B) Protonated section of the present dithizonate anion.

four contacts to the potassium ion are also two pairs of "chelate" type interactions, originating in S,N(B2) combinations, the associated K···H(B6) distances are longer (greater than 3.1 Å) and less relevant. About the sulfur atom, a pair of symmetry related potassium ions is found (S···K(1/2−x, y−1/2, z), (x, 1/2−y, 1/2+z), 3.150 (2), 3.426 (3) Å), with the angle subtended at the sulfur being 80.83 (5)° and K···K, 4.268 (2) Å).

The "acidic" hydrogen atom of the anion is clearly associated with N(A2); as refined, the angles H–N(A2)–N(A1), C(A1) may be slightly unsymmetrical (113(3), 125(3)°) with H···S, 2.34 (5), and H···H(A6), 2.4 Å. The *cis* angles at N(A1) and C(A1) are 114.9 (4), 118.0 (5), slightly greater than their counterparts in section B (114.6(4); 115.5(5)°), with the presence of H presumably a contributing factor, as it also presumably is to the distortions noted above in section A.

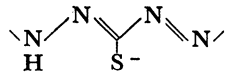
In considering geometry and bonding within the ligand, (Table 3), the closest analogues with which comparison might usefully be made appear to be (i) the protonated ligand (2),⁶⁾ with a pair of similar halves (average geometry quoted), and (ii) the five-coordinate indium(III) complex, (3),³⁾ in which a pair of chelating ligands are found with distinctly different geometries for the chelating segment, denoted (A) and the non-chelating (B), and a third ligand which is monodentate S-coordinated, with a protonated section (denoted (B)) and an unprotonated section (A). The geometries of these species are compared in Table 4 with those of sections A and B of the present anion. With certain dimensional exceptions, the present values are comparable with others expected to lie at the extremes of the range. The exceptions are:

(i) The carbon–sulfur distance, comparable with that in the free ligand, but shorter than that in the S-coordinated monodentate ligand of the indium complex (3), and, in parallel, because of electron-pair repulsion effects

(ii) The N–C–N angle again resembles more nearly the value of the free ligand, rather than that of the S-coordinated monodentate ligand;

(iii) The C–N–NH angle in the present complex is less than its counterpart in the protonated section of the monodentate ligand of the indium complex, and nearer the value of the free ligand, presumably assisted by the incorporation of the potassium ion on its opposite side.

The two halves of the ligand suggest a considerable contribution of the resonance form



The length of certain bonds, in particular, C–S, (1.719(5) Å) and N(A2)–C(A1), 1.382(7) Å, are indicative of more extensive delocalization, however. A number of non-hydrogen interanion contacts, generated in the stacking apparent in Fig. 1(a) by (x, 1/2−y, 1/2+z), approach 3.3 Å as a lower limit and are suggestive of the possibility of charge-transfer interactions.

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