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Short Communication

A polymeric 1:2 adduct of barium thiocyanate with pyridine betaine, $Ba(C_5H_5NCH_2CO_2)_2(NCS)_2$

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Abstract

The 1:2 adduct of barium thiocyanate with pyridine betaine (pyridinioacetate) crystallizes in the monoclinic space group $C2/c$ with $Z=4$, $a=26.858(4)$, $b=8.433(2)$, $c=8.729(1)$ Å and $\beta=90.67(1)°$; the structure has been refined to $R=0.027$ for 1982 observed Mo Kα data. The complex features a polymeric zigzag chain in which adjacent barium atoms are linked by a pair of centrosymmetrically-related carboxylato-μ-O-η-O,O′ bridges. The barium atom occupies a site of symmetry 2, being coordinated by pairs of chelating pyridine betaine, μ-O bridging pyridine betaine, and N-bonded thiocyanate ligands in an approximate dodecahedral arrangement.

Introduction

The binding of calcium to carboxylates has been extensively studied by Einspahr and Bugg [1], who noted that a simple carboxylate can function as either a monodentate or a bidentate chelate ligand. Calcium and barium binding with dicarboxylates, especially malonates [2, 3], have attracted much attention recently. The α-substituted malonate derivatives are modeled to elucidate the binding of the amino acid residues γ-carboxyglutamic and β-carboxyaspartic acids to calcium [4–6] and barium [7, 8] in both blood and bone proteins. On the other hand, the crystal structures of only a few barium(II) monocarboxylates and related complexes are known. The carboxylate group is monodentate in $Ba(CH_3CO_2)_2[N(CH_2CH_2OH)_3]_2$ [9], while the μ-O-η-O,O′ mode is found in $BaNpO_2(CH_3CO_2)_3 \cdot 2H_2O$ [10] in which the two carboxylate oxygens chelate to the neptunyl atom and one oxygen forms a bridge between it and the barium atom.

In recent studies we have shown that betaine (trimethylammonioacetate) and its derivatives, considered as structural analogues of the amino acids which can take a zwitterionic form containing positively charged quarternary ammonium and anionic carboxylate moieties, can form stable and soluble complexes with various transition metals. The overall charge neutrality of betaines enables metal–betaine complexes to bear additional anionic ligands, and the stoichiometric ratio can be varied subject to steric limitation. Furthermore, the considerable coordinative flexibility and large ionic radius of the barium(II) atom is conductive to its binding with carboxylate groups, thus providing a rationale to our attempted synthesis of adducts of barium thiocyanate with betaine derivatives. As a sequel to previous studies of calcium–betaine complexes such as $Me_3NCH_2CO_2 \cdot CaCl_2 \cdot 2H_2O$ [11] and $[CaCu(Me_3NCH_2CO_2)_4(NO_3)_2(H_2O)]_2\{[Ca(NO_3)_4(H_2O)]_2\}$ [12], in which the carboxylate groups of the betaine ligand bind to calcium in the bridged mode only, we have now prepared the first example of a barium–betaine complex, *catena*-di(thiocyanato-*N*)-bis(μ-pyridinioacetato-*O*)barium(II), $Ba(C_5H_5NCH_2CO_2)_2(NCS)_2$, and characterized it by single crystal X-ray analysis.

Experimental

Preparations

Anhydrous pyridine betaine (pyridinioacetate) was prepared according to the method reported previously [13]. ^{1}H NMR data: δ 5.28 (2H, s, CH_2), 8.11 (2H, t, *m*-H-py), 8.62 (1H, t, *p*-H-py), 8.83 (2H, d, *o*-H-py).

Barium thiocyanate (BDH) was recrystallized from aqueous ethanol and dehydrated under vacuum to give a white powder. Anhydrous $Ba(SCN)_2$ (250 mg, 0.99 mmol) and pyridine betaine (230 mg, 1.68 mmol) were each dissolved in *c.* 10 ml warm absolute methanol. The methanolic solution of pyridine betaine was added dropwise to the $Ba(SCN)_2$ solution without agitation. Colorless, cuboid crystals of the complex $Ba(C_5H_5NCH_2CO_2)(NCS)_2$ were grown at room temperature by slow evaporation of the colorless solution overnight. They were collected and air-dried, and are stable in air for a prolonged period.

The density of the crystal was measured by flotation in $CCl_4/BrCH_2CH_2Br$. The ^{1}H NMR spectrum was recorded on a Brucker WM250 spectrometer at 250

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MHz using D_2O as solvent, and chemical shifts were in δ_H (ppm) downfield from an internal DSS standard. IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 205 FTIR spectrometer.

X-ray crystallography

Intensity data were collected in the ω-scan mode [14] on a Nicolet R3m/V X-ray diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Crystal stability was monitored by two check reflections every 125 measurements and no significant decay was observed. The data were corrected for Lorentz and polarization factors, and empirical absorption corrections based on an ellipsoidal fit to Ψ-scan data [15] were applied. The learnt-profile technique [16] was employed to process the raw intensities. Crystallographic details concerning the data collection and reduction, as well as the structure analysis, are presented in Table 1.

The structure was solved by Patterson methods and refined by full matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the pyridine betaine ligand were generated in their idealized positions, assigned fixed isotropic temperature factors (0.08 $Å^2$), and included in the calculation of structure factors.

All calculations were performed on a DEC MicroVax II computer using the SHELXTL PLUS program package [17]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [18]. Final atomic coordinates and equivalent isotropic temperature factors are tabulated in Table 2. Significant bond lengths and angles in the complex are listed in Table 3.

Results and discussion

The COO IR absorption bands (cm^{-1}) of the barium complex ($\nu_{as} = 1599$vs,br; $\nu_s = 1378$vs, 1393vs) are significantly different from those of pyridine betaine ($\nu_{as} = 1635$vs; $\nu_s = 1377$vs) [19, 20]. These differences indicate that the carboxylato oxygens are bound to the

TABLE 1. Data collection and processing parameters

Molecular formula	$Ba(NCS)_2(C_5H_5NCH_2CO_2)_2$
Molecular weight	527.80
Color and habit	colorless cube
Unit cell parameters	
a (Å)	26.858(4)
b (Å)	8.433(2)
c (Å)	8.729(1)
β (°)	90.67(1)
V ($Å^3$)	1977.17(4)
Z	4
F (000)	1032
Density (meas.) ($g\ cm^{-3}$)	1.79
Density (calc.) ($g\ cm^{-3}$)	1.77
Space group	$C2/c$ (No. 15)
Radiation	graphite-monochromatized Mo Kα, $\lambda = 0.71073$ Å
Standard reflections	(7,3,3), (4,2,3)
Intensity variation (%)	±2
R_{int} (from merging of equiv. reflections)	0.011
Absorption coefficient (cm^{-1})	22.38
Crystal size (mm)	0.50×0.48×0.24
Mean μr	0.455
Transmission factors	0.222 – 0.280
Scan type and rate (° min^{-1})	ω-scan; 3.21 – 14.65
Scan range	0.70° below Kα_1 to 0.70° above Kα_2
Background counting	stationary counts for one-half of scan time at each end of scan range
Collection range	$h,k,\pm l$; $2\theta_{max} = 55°$
Unique data measured	2205
Obs. data with $\|F_o\| \geq 6\sigma(\|F_o\|)$, n	1982
No. of variables, p	131
$R_F = \Sigma\|\|F_o - \|F_c\|\|/\Sigma\|F_o\|$	0.027
Weighting scheme	$w = [\sigma^2(F_o) + 0.0005\|F_o\|^2]^{-1}$
$R_G = [\Sigma w(\|F_o\| - \|F_c\|)^2/\ \Sigma w\|F_o\|^2]^{1/2}$	0.048
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	1.781
Residual extrema in final difference map (e $Å^{-3}$)	−0.614 to +0.651

TABLE 2. Atomic coordinates ($\times 10^5$ for Ba; $\times 10^4$ for other atoms)

Atom	x	y	z	U_{eq}
Ba(1)	0	6929(3)	25000	311(1)
S(1)	−2037(1)	44(2)	2014(2)	72(1)
O(1)	−43(1)	−1835(3)	4436(3)	45(1)
O(2)	−390(1)	−3501(4)	6088(3)	52(1)
N(1)	−1024(2)	297(7)	2470(8)	86(2)
N(2)	−1119(1)	−4354(3)	4096(4)	39(1)
C(1)	−1443(2)	178(5)	2287(6)	51(1)
C(2)	−348(2)	−2913(4)	4788(3)	36(1)
C(3)	−681(2)	−3538(5)	3491(4)	43(1)
C(4)	−1495(2)	−3485(6)	4676(6)	56(1)
C(5)	−1891(2)	−4216(7)	5342(8)	66(2)
C(6)	−1909(2)	−5846(7)	5413(7)	64(2)
C(7)	−1520(2)	−6713(6)	4826(6)	67(2)
C(8)	−1129(2)	−5946(5)	4166(6)	53(1)

[a] U_{eq} defined as one third of the trace of the orthogonalized U tensor.

TABLE 3. Bond lengths (Å) and bond angles (°)

Ba(1)-N(1)	2.770(5)	Ba(1)-O(1)	2.724(3)
Ba(1)-O(1a)	2.844(3)	Ba(1)-O(2a)	2.862(3)
S(1)-C(1)	1.613(5)	N(1)-C(1)	1.140(7)
O(1)-C(2)	1.263(5)	O(2)-C(2)	1.244(4)
C(2)-C(3)	1.529(5)	N(2)-C(3)	1.467(5)
N(2)-C(4)	1.350(6)	N(2)-C(8)	1.344(5)
C(4)-C(5)	1.364(8)	C(5)-C(6)	1.378(8)
C(6)-C(7)	1.380(8)	C(7)-C(8)	1.366(8)
O(1)-Ba(1)-N(1)	82.1(1)	O(1)-Ba(1)-O(1a)	71.5(1)
N(1)-Ba(1)-O(1a)	94.5(2)	O(1)-Ba(1)-O(1b)	77.0(1)
N(1)-Ba(1)-O(1b)	87.1(1)	O(1)-Ba(1)-O(1c)	147.9(1)
N(1)-Ba(1)-O(1c)	90.2(2)	O(1a)-Ba(1)-O(1c)	140.4(1)
O(1)-Ba(1)-O(2a)	113.5(1)	N(1)-Ba(1)-O(2a)	117.5(1)
O(1a)-Ba(1)-O(2a)	45.9(1)	O(1)-Ba(1)-O(2c)	153.8(1)
N(1)-Ba(1)-O(2c)	74.8(1)	O(1a)-Ba(1)-O(2c)	97.8(1)
O(2a)-Ba(1)-O(2c)	68.3(1)	N(1)-Ba(1)-N(1b)	166.2(2)
Ba(1)-N(1)-C(1)	172.3(5)	Ba(1)-O(1)-C(2)	138.2(2)
C(2)-O(1)-Ba(1a)	92.0(2)	C(2)-O(2)-Ba(1a)	91.5(2)
S(1)-C(1)-N(1)	178.9(5)	O(1)-C(2)-O(2)	125.0(3)
O(1)-C(2)-C(3)	116.3(3)	O(2)-C(2)-C(3)	118.6(3)
C(3)-N(2)-C(4)	119.1(3)	C(3)-N(2)-C(8)	120.0(4)
C(4)-N(2)-C(8)	120.7(4)	N(2)-C(3)-C(2)	111.1(3)
N(2)-C(4)-C(5)	120.3(4)	N(2)-C(8)-C(7)	120.5(5)
C(4)-C(5)-C(6)	119.9(5)	C(5)-C(6)-C(7)	119.0(5)
C(6)-C(7)-C(8)	119.7(5)		

Symmetry transformation: a $(-x, -y, 1-z)$, b $(-x, y, \frac{1}{2}-z)$, c $(x, -y, z-\frac{1}{2})$.

barium atom to different extents. The separations Δ ($=\nu_{as}(COO)-\nu_s(COO)$) in the complex are 206 and 221 cm^{-1}, which are much less than that (258 cm^{-1}) in pyridine betaine. The smaller Δ values are consistent with their assignment to bridging and/or chelating mode(s) of carboxylate groups [21]. Moreover, the relatively small value of 2051 cm^{-1} for ν(C–N) and large value of 849 cm^{-1} for ν(C–S) are indicative of a terminal N-bound thiocyanate ligand rather than an end-to-end bridged one.

The asymmetric unit in the crystal structure corresponds to the empirical formula $Ba(C_5H_5NCH_2CO_2)_2(NCS)_2$. The barium atom lies on a crystallographic two-fold axis. Each pair of adjacent barium atoms, related by an inversion centre and separated by a non-bonded distance of 4.518(1) Å, are bridged by the carboxylato-O groups from two centrosymmetric-related pyridine betaines to form a four-membered Ba_2O_2 ring (Fig. 1). The resulting polymeric zigzag chain extends in the direction of the c axis.

As can be seen in Fig. 1, the barium ion is eight-coordinate in the complex, the ligand sites being occupied by six oxygen atoms from four pyridine betaines and two nitrogen atoms from two terminal thiocyanate ligands. The geometry at barium can be described as a distorted form of the D_{2d} dodecahedron found in the classical $[Mo(CN)_8]^{4-}$ ion [22].

Every barium atom binds to four different pyridine betaine ligands through μ-O bridges (two Ba–O = 2.724(3) Å) and η-O,O′ interactions (two Ba–O = 2.844(3) Å and two Ba–O = 2.862(3) Å). The carboxylate group in the present complex thus acts in the very unusual carboxylato-η-O,O′ chelating plus μ-O bridging mode, which is quite rare among metal carboxylates [23–25], and only three examples have been found among metal complexes of betaines. This uncommon binding mode seems to occur when the carboxylate groups of betaines coordinate to metal ions of large radii such as mercury(II) [13], cadmium(II) [26] and barium(II) (this work).

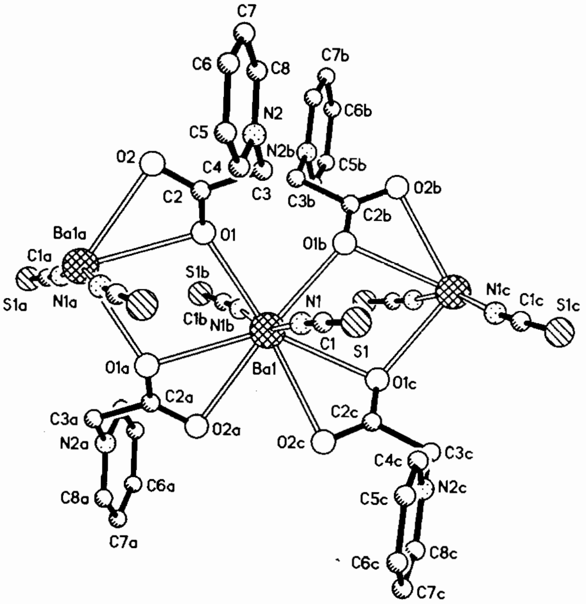

Fig. 1. Perspective view showing the coordination environment of the Ba(1) atom in the complex $Ba(C_5H_5NCH_2CO_2)_2(NCS)_2$ and the atom numbering scheme. Symmetry transformation is given in Table 3.

TABLE 4. The O–C–O angles (°) of betaine derivatives of some metal complexes in bidentate chelate mode

Compound[a]	O–C–O angle	Binding mode	Reference
$[Cd(bet)(H_2O)Cl_2]_2$	123.9(1)	bidentate chelate	28
$Cd_3(bet)_4(SCN)_6(H_2O)_2$	123.8(3)	bidentate chelate	26
$Cd(prbet)(NCS)_2$	121.9(3)	carboxylato-μ-O-η-O,O′ bridge	26
$Ba(pybet)_2(NCS)_2$	125.0(3)	carboxylato-μ-O-η-O,O′ bridge	this work
$[Hg(pybet)_2Cl_4 \cdot HgCl_2]_n$	127(2)	carboxylato-μ-O-η-O,O′ bridge	13

[a] bet = betaine (IUPAC: trimethylammonioacetate), $(CH_3)_3NCH_2CO_2$; pybet = pyridine betaine (IUPAC: pyridinioacetate), $C_5H_5NCH_2CO_2$; prbet = propyl betaine (IUPAC: trimethylammoniopropanoate), $(CH_3)_3NCH_2CH_2CO_2$.

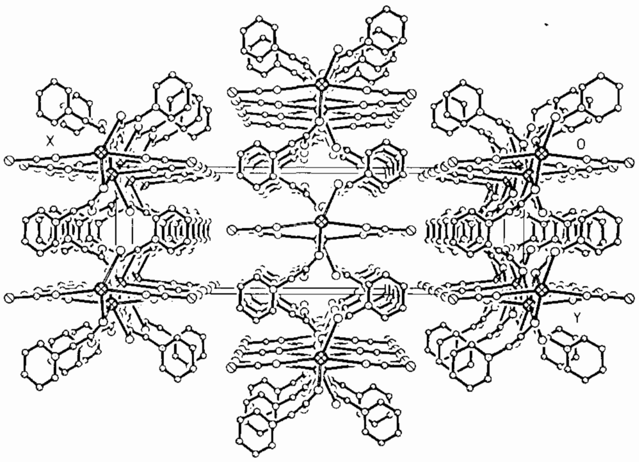

Fig. 2. Molecular packing in the crystal structure of $Ba(C_5H_5NCH_2CO_2)_2(NCS)_2$. The origin of the unit cell lies at the upper right corner, with *a* pointing from right to left, *b* downwards, and *c* towards the reader.

The $Ba(NCS)_2$ moiety is non-linear (N(1)–Ba(1)–N(1b) = 166.2(2) Å) and bends towards the μ-O carboxylato groups as a result of the greater steric repulsion of the η-O,O′ bidentate chelating pyridine betaines (Fig. 1). The chelate ring of the carboxylate group is slightly twisted out of the plane of its neighboring Ba_2O_2 ring, making a dihedral angle of 160.9(1)° with respect to the shared Ba(1)–O(1a) edge.

The Ba–O bond lengths in the complex range from 2.724(3) to 2.862(3) Å, which are in good agreement with the values observed in previous studies of related compounds [7–10, 27]. The shortest bond involves the μ-O linked carboxylato oxygen (Ba(1)–O(1) = 2.724(3) Å) while the longest bond is formed by the carboxylato oxygen solely engaged in monodentate interaction (Ba(1)–O(2a) = 2.862(3) Å).

As might be expected, the μ-carboxylato oxygen O(1) weakens its associated C–O bond to a greater extent than does the monodentate oxygen O(2). The C(2)–O(1) (1.263(5) Å) and C(2)–O(2) (1.244(4) Å) bond lengths are significantly different but intermediate between the usual C–O single and double bond values. It is noteworthy that pyridine betaine, with its large ligand bite (O–C–O = 125.0(3)°), reflecting the considerable inductive effect of the positively charged pyridinium moiety as found in the case of mercury(II) complexes [13], chelates to barium in view of the large ionic size of the latter. The O–C–O angles in other metal complexes containing betaine derivatives acting in the bidentate chelate mode are compared in Table 4, noting that these values cover a fairly large range (121.9(3)–127(2)°).

The crystal structure of the present complex is illustrated in Fig. 2. Along each polymeric chain parallel to the *c* axis, the pyridine rings are stretched out away from the backbone to minimize their mutual steric hindrance. For each pair of adjacent chains related by the *b* translation, the pyridine rings fit together in an interlocking manner to form stacked columns running parallel to the chain axis. The π interaction between the nearly exactly overlapping and parallel aromatic rings undoubtedly plays a significant role in conferring stability to the molecular packing. Interaction between neighboring chains in the *a* direction is of the van der Waals type.

The present structural study shows that, owing to its large ionic radius, the binding of barium to betaines can be in the bidentate chelate mode even when the O–C–O angle becomes quite large. On the other hand, although calcium possesses the ability to adopt a wide variety of coordination geometries like barium, hitherto only *syn–syn* bridged carboxylate binding [11, 12] has been found. Hence unusual coordination and variable binding modes are expected to occur in betaine complexes of metals with large ionic radii, and further investigations along this line are in progress.

Supplementary material

Tables of anisotropic temperature factors, hydrogen coordinates, and a list of observed and calculated structure factors (11 pages) are available from author T.C.W.M. on request.

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