Notes

Crystal Structure and Magnetic Properties of Bis(N,N-dimethyl-2-thiophenemethylammonium) Tetrabromocobaltate(II)†

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Considerable interest has been shown over recent years in the transition metal halide complexes, and, among them, the tetrahalometalates with various organic countercations have been the subject of theoretical,[1-3] structural,[4-8] magneto-structural[9-14] and spectroscopic[15-17] studies. The magneto-structural relation in the tetrabromocuprate with various organic countercations has been intensively studied, and in view of the magnetic properties of these compounds, the Br⋯Br contact and the Cu-Br-Cu bridge are known to be quite important;[18,19] the antiferromagnetic coupling in the series of tetrabromocuprate compounds is produced *via* a 'two-halide' Cu-Br⋯Br-Cu contact while the ferromagnetic coupling is through a 'single-halide' Cu-Br-Cu bridge. The hydrogen bonding[20,21] and noncovalent π-interaction between the aromatic rings of organic cations[13,22] in this type of molecules control molecular recognitions and self-assembly processes, and exercise important effects on the solid-state structure and the properties of many compounds relevant to biological and material sciences.[23-25] Despite the structural similarities between the tetrabromocuprates and the tetrabromocobaltate complexes, the magneto-structural studies for the tetrabromocobaltate complexes and other cobalt(II) compounds have been rarely reported.

In this work, we report the crystal structure and magnetic behaviors of the $(dmamtH)_2CoBr_4$ complex. The 2-(N,N-dimethylaminomethyl)thiophene (dmamt) base contains an amine group and an aromatic thiophene ring, and therefore we expected that the protonated base $dmamtH^+$ as a cation might play an important role in stabilizing the solid-state structure of the $(dmamtH)_2CoBr_4$ complex. The magnetic behavior of the $(dmamtH)_2CoBr_4$ complex was investigated to confirm the importance of the Br⋯Br separation for two-bromide super-exchange pathways in the complex.

Experimental Section

The $(dmamtH)_2CoBr_4$ was prepared from a direct reaction between 2-(N,N-dimethylaminomethyl)thiophene·HBr, (dmamtH)Br and anhydrous cobalt(II) bromide. The (dmamtH)Br salt was prepared from a reaction of 2-(N,N-dimethylaminomethyl)thiophene (dmamt) (6 mmol) with an excess of concentrated hydrobromic acid in 50 mL of ethanol-triethylorthoformate mixture solvent (5 : 1 v/v). 3 mmol of cobalt(II) bromide was dissolved in 10 mL of ethanol-triethylorthoformate (5 : 1 v/v). This solution was added into a (dmamtH)Br solution. The solution was heated with stirring for 5 h, and then allowed to cool in an ice bath. The precipitates were isolated by filtration and washed with cold ethanol. The blue single crystals were obtained by recrystallization in acetonitrile. The yield of the product was 1.38 g (69.38%) based on $CoBr_2$. Anal. Calcd. for $CoC_{14}H_{24}Br_4N_2S_2$: C, 25.36; H, 3.65; N, 4.23; S, 9.67. Found: C, 25.31; H, 3.66; N, 4.19; S, 9.72. All manipulations were carried out in an open atmosphere.

The magnetic susceptibility measurements were made on a powered polycrystalline sample over the temperature range of 6 K to 300 K with a Quantum Design MPMS-7-SQUID susceptometer. The data was corrected for the diamagnetism of the constituent atoms with Pascal's constant.

The data for X-ray structure determination were collected on a Siemens P4 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The unit cell dimensions were determined on the basis of 40 reflections in the range of $4.5^o < \theta < 13.0^o$. The data were collected by the ω-2θ technique. Empirical absorption correction was applied to the intensity data. The standard direct method was used to position the heavy atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically except the three disordered carbon atoms on the 5-membered rings which were refined isotropically. All hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms (B_{iso} =

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$1.2B_{eq}$ or $1.5B_{eq}$). The structure was refined in a full matrix least-squares calculation on F^2. All the computations were carried out with the SHELX-97 program package.[26] Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-186168). The data can be obtained free of charge *via www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The crystallographic and the molecular structure of the $(dmamtH)_2CoBr_4$ determined and details of data collection and structural refinements for the complex are given in Table 1. The molecular geometry and thermal ellipsoids along with the numbering schemes are shown in Figure 1, and the selected bond distances and angles are listed in Table 2. The crystal structure of the $(dmamtH)_2CoBr_4$ complex consists of discrete $CoBr_4^{2-}$ anions and $dmamtH^+$ cations held together by the N-H···Br hydrogen bonding. The two Co-Br distances [2.439(3) and 2.431(3) Å] involved in the hydrogen bonding are slightly longer than the other two Co-Br distances [2.404(3) and 2.387(3) Å] and the slight elongation of these bond distances is presumably due to a reduction of electron density on the bromide ions. The Br-Co-Br bond angles vary within the range 106.19(10)-114.11(11)°. The average bond angle of Br-Co-Br is 109.4° and the average dihedral angle between two Br_2Co planes is 87.7° as the $CoBr_4^{2-}$ unit maintains a nearly perfect tetrahedral geometry around the Co atom. The hydrogen bond distances and bond angles along with the dihedral angles between two Br_2Co planes are summarized in Table 3. There are no important bonding interactions between tetrabromo-

Table 1. Crystallographic data of $(dmamtH)_2CoBr_4$

	$(dmamtH)_2CoBr_4$
Chemical formular	$CoC_{14}H_{24}N_2S_2Br_4$
FW (amu)	663.04
Crystal description	Blue Irregular
Crystal size (mm)	$0.30 \times 0.30 \times 0.20$
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
T(K)	293(2)
Radiation(Mo Kα) (λ/Å)	0.71073
a (Å)	9.460(1)
b (Å)	18.070(5)
c (Å)	13.9139(2)
β (°)	100.34(1)
V (Å^3)	2339.7(8)
Z	4
$d_{calcd.}$ (Mg m^{-3})	1.882
Absorption coefficient, μ (mm^{-1})	7.743
F (0 0 0)	1284
θ range for data collection (°)	1.87 to 25.00
Index ranges	$-1 \leq h \leq 11$, $-21 \leq k \leq 1$, $-16 \leq l \leq 16$
Reflections collected/unique	5274/4127 [R(int) = 0.0733]
Absorption Correction	Psi-scan
Max. and min. transmission	0.417 and 0.163
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4127 / 0 / 232
Goodness of fit	1.061
Final R indices [I > 2σ(I)]	$R_1 = 0.0785^a$, $\omega R_2 = 0.1596^b$
Extinction coefficient	0.0041(5)
Largest diff. peak and hole (eÅ^{-3})	0.785 and -0.887

$^aR_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$. $^b\omega R_2 = [\Sigma_\omega(F_o^2-F_c^2)^2/\Sigma_\omega(F_o^2)^2]^{1/2}$.

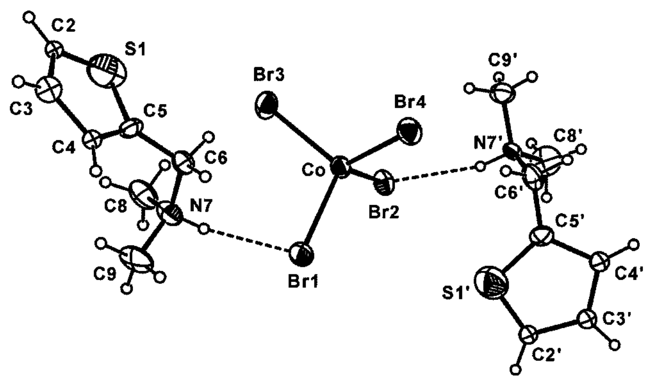

Figure 1. *ORTEP-3* diagram of $(dmamtH)_2CoBr_4$ with hydrogen bonding showing the atom-numbering scheme and 30% probability ellipsoids.

Table 2. Selected bond lengths (Å) and angles (deg) for the $(dmamtH)_2CoBr_4$

Co-Br1	2.439(3)	N7'-C8'	1.49(2)
Co-Br2	2.431(3)	N7-C9	1.48(2)
Co-Br3	2.404(3)	N7'-C9'	1.49(2)
Co-Br4	2.387(3)	C2-C3	1.54(4)
S1-C2	1.62(2)	C2'-C3'	1.50(3)
S1'-C2'	1.56(2)	C3-C4	1.45(3)
S1-C5	1.726(15)	C3'-C4'	1.43(4)
S1'-C5'	1.679(17)	C4-C5	1.60(2)
N7-C6	1.512(18)	C4'-C5'	1.55(2)
N7'-C6'	1.525(19)	C5-C6	1.494(19)
N7-C8	1.46(2)	C5'-C6'	1.47(2)
Br4-Co-Br3	114.11(11)	C3-C2-S1	112.9(16)
Br4-Co-Br2	108.80(10)	C3'-C2'-S1'	110.0(18)
Br3-Co-Br2	106.19(10)	C4-C3-C2	116(2)
Br4-Co-Br1	109.02(11)	C4'-C3'-C2'	117(2)
Br3-Co-Br1	108.05(10)	C3-C4-C5	100.8(18)
Br2-Co-Br1	110.66(10)	C3'-C4'-C5'	101.6(17)
C2-S1-C5	94.0(11)	C4-C5-S1	115.9(12)
C2'-S1'-C5'	97.8(12)	C4'-C5'-S1'	113.2(12)
C8-N7-C6	112.0(14)	C6-C5-S1	119.4(12)
C8'-N7'-C6'	115.9(15)	C6'-C5'-S1'	124.7(12)
C8-N7-C9	113.4(17)	C6-C5-C4	124.7(13)
C8'-N7'-C9'	111.6(14)	C6'-C5'-C4'	122.1(15)
C9-N7-C6	112.0(14)	C5-C6-N7	115.5(12)
C9'-N7'-C6'	110.2(14)	C5'-C6'-N7'	111.8(13)

Table 3. Dihedral angles (°) between A and B planes, and hydrogen bonding for the $(dmamtH)_2CoBr_4$

A	B		Dihedral Angles (°)	
Br1-Co-Br2	Br3-Co-Br4		89.40(8)	
Br1-Co-Br3	Br2-Co-Br4		86.61(7)	
Br1-Co-Br4	Br2-Co-Br3		87.21(7)	
Hydrogen bonding mode	N-H (Å)	H···Br (Å)	N···Br (Å)	∠N-H-Br (°)
N7-H7···Br1	0.910	2.419	3.314	167.91
N7'-H7'···Br2	0.910	2.475	3.336	157.96

cobaltate anions; the nearest nonbonded Co···Br distance is 6.293 Å and there is no single-bromide bridge of the type Co-Br-Co. However, there are two relatively short Co-Br··· Br-Co contact pathways; the shortest Br···Br contact of 4.465 Å (Br2···Br1') in the structure is 0.6 Å longer than the sum of the bromine ion van der Waals radii (3.9 Å). The two bromine atoms in this pathway are also involved in the hydrogen bonding interaction, and the tortional angle of Co-Br···Br-Co plane is -33.6°. The second shortest Br···Br contact of 4.660 Å (Br4···Br4'') is ~0.8 Å longer than van der Waals radii, but two cobalt and two bromine atoms are on the same plane with the Co-Br···Br angle of 140.59°. The distance between two Co atoms is 8.882 Å. The aromatic thiophene ring of the cation is nearly perfectly planar and two adjacent thiophene rings are strictly parallel, face to face stacked with an interplanar distance of *ca*. 3.48 Å, indicating the presence of π-interaction between the aromatic thiophene rings. These rings are offset one from another by 2.34 Å with a staggered orientation. There is an inversion center i (= S_2) at the center of the cavity produced by an array of $dmamtH^+$ cations and $CoBr_4^{2-}$ anions as it is shown in Figures 2 and 3b.

The Br···Br contact distances of 4.465 and 4.660 Å might be short enough to allow the magnetic super-exchange to occur antiferromagnetically between two paramagnetic cobalt(II) centers of two different $CoBr_4^{2-}$ anions. The unpaired electron density in 3d metal ions is substantially delocalized out on to the 4p orbitals of the bromide ion due to the small energy difference between them.[9,15] Previous workers reported the presence of a weak antiferromagnetic super-exchange *via* Co-O···O-Co contact in $[Co(C_5H_5NO)_6]$-$[NO_3]_2$ where the distance of the O···O contact is 5.53 Å.[27] This type of the magnetic exchange pathway with the Br···Br contact distances of 3.80-4.55 Å is well established experimentally and theoretically for the tetrabromocuprate compounds.[3,12,18,28] The strength of these interaction, which are invariable antiferromagnetic, decreases rapidly with the Br···Br distance.[14]

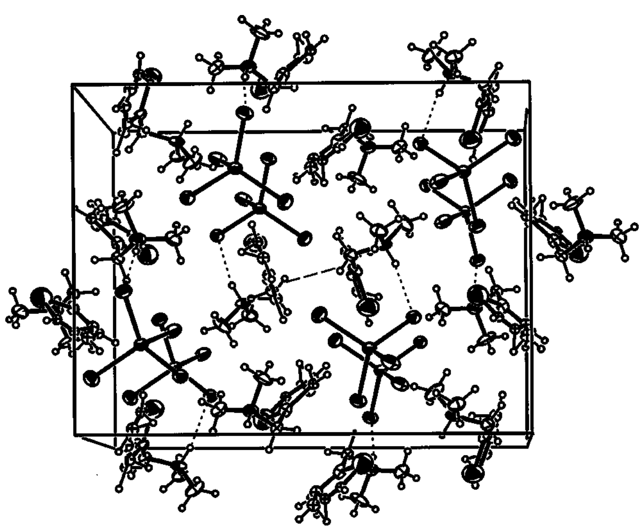

Figure 2. A molecular packing diagram along with (100) plane in a unit cell for $(dmamtH)_2CoBr_4$ showing 30% probability ellipsoids. Intermolecular hydrogen bonds are shown with short-dashed lines and a π-π stacking interaction between two thiophene rings is denoted by long-dashed line.

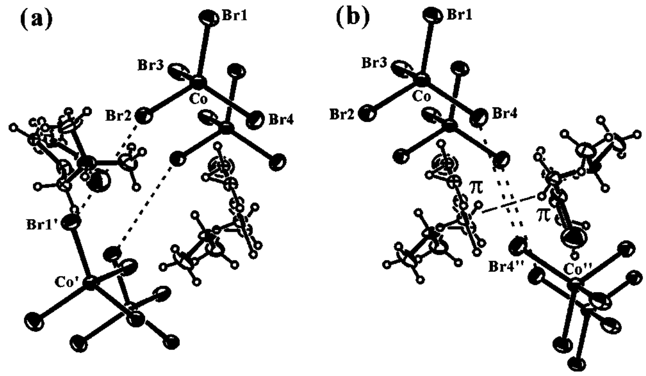

Figure 3. The two possible magnetic super-exchange pathways in a unit cell [(100) plane] for the $(dmamtH)_2CoBr_4$ complex. The 30% probability ellipsoids are used. The Br···Br contacts are shown with short-dashed lines. And a π-π stacking interaction is shown in the same way as in Figure 2.

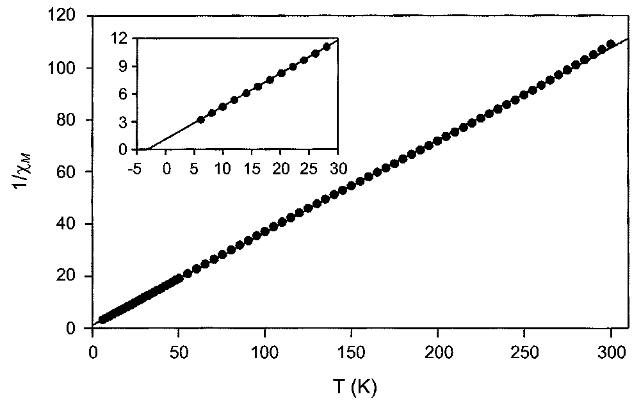

Figure 4. A plot of temperature against the reciprocal magnetic susceptibility of $(dmamtH)_2CoBr_4$.

The room temperature magnetic moment of the $(dmamtH)_2$-$CoBr_4$ complex is 4.69 BM and is typical for noninteracting or weak interacting high spin d^7 cobalt ions. The effective magnetic moments were calculated by $\mu_{eff} = 2.828(\chi_M \times T)^{1/2}$. As the temperature is lowered, the effective magnetic moment is practically constant down to about 20 K, but it decreases upon further cooling from 20 K to 6 K (μ_{eff} = 4.41 BM at 20 K and 3.86 BM at 6 K). Magnetic susceptibility data of the $(dmamtH)_2CoBr_4$ are well described by the

Curie-Weiss law, $\chi_M = C/(T-\theta)$, with a negative temperature intercept (θ) of -3.14 K and a slope corresponding to a Curie constant of C = 2.81 cm^3Kmol^{-1} as it is shown in Figure 4.

Conclusion

The crystalline structure of $(dmamtH)_2CoBr_4$ is stabilized by the intramolecular hydrogen bonding interaction and the π-interaction between aromatic thiophene rings stacked in the parallel fashion. These interactions also provide two relatively short Co-Br···Br-Co contact pathways in the solid-state structure of the complex. The decrease in the effective magnetic moment upon cooling from 20 K to 6 K, and the negative value of Curie-Weiss constant θ suggest the presence of weak anti-ferromagnetic interactions in this complex. Based on the structural data described above, it is reasonable to suggest that the possible magnetic super-exchange pathways are two Co-Br···Br-Co contacts denoted by pathway (a) or pathway (b) in Figure 3.

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