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Synthesis and Structural Characterization of Polyiodide and Mixedpolyhalide ions with Transition Copper Metal Cation

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Abstract: *Synthesis and structural characterization of polyiodide and mixed polyhalide complex of copper (II) having formula* ***$[Cu(phen)_3](I_4Br_4)_{0.5}(IBr_2)$*** *,Reaction of $CuBr_2$,1,10-phenantroline , iodine and bromine ,have been described . Reaction of 1: 3 :2 :5 (of $CuBr_2$, 1,10-phenantroline, iodineand bromine) produce complex in 72 % yield The complex was characterized by analytical spectroscopic and molecular structure of the complexwas determined by X-ray crystallography .*

Keywords : ***$[Cu(phen)_3](I_4Br_4)_{0.5}(IBr_2)$*** *,X-ray crystallography .*

I. Introduction

The polyhalide species (iodides, bromides and iodobromides) have been synthesized as salts of inorganic or organic cations, because of their interesting structural variety and unusual physical properties.[1]Everypolyhalide ion contains halogen molecules (X_2) acting as Lewis acid (acceptor) and halide ions (X^-) acting as Lewis base (donar).These are the fundamental building blocks of polyhalides with different shape of structure and their complexity. Among all known polyhalides, the chemistry of the iodine compounds has long been known and large number of polyiodide anions have been structurally characterized in the range of I_3^- to I_{29}^- with infinite–chain and layer type networks.The Lewis acid acceptor iodine and the Lewis base donors I^- or I_3^- can be regarded as the fundamental "building blocks" of polyiodides. The stability of the polyiodide anion is largely dependent on the cation chosen. It has been found that most stable salts are formed when the cation and anion are of nearly same size.

A limited number of polybromide anions have also been reported: Br_3^-, Br_4^{2-}, Br_8^{2-}, Br_{11}^-, Br_{20}^{2-} and Br_{24}^{2-}.[4, 5] Consequently,these reported polybromides are used in carbon nanotube modification, battery technology, and synthetic chemistry.[6,7] However, our understanding of the factors that control polybromide is still significantly less well developed than it is for polyiodide. It should be noted that polyiodides and polybromides of the same couterion exhibit the same kind of polyhalide structure in all instances reported to date.[8]With regard to I–Br mixed polyhalide anions, five different types (I_2Br^-/IBr_2^-,[9,10]$I_2Br_3^-$,[11]IBr_4^-,[12]and $I_3Br_4^-$[10c,13]) mono anions and one dianion ($I_2Br_6^{2-}$)[12] have been reported. Out of the five mono anions, tri-iodobromide (IBr_2^-or I_2Br^-) anion has reported in huge numbers with different cations.[9,10]

II. Experimental Section

2.1. Materials: All chemicals (metal acetates, metal bromides, 1, 10–phenanthroline, 2, 2'–bipyridyl, potassium iodide, iodine, bromine, acetonitrile and DCM) were of reagent grade obtained from commercial sources and were used without further purification.

2.2 .$[Cu(phen)_3](I_4Br_4)_{0.5}(IBr_2)$ (4):$CuBr_2$ (0.225 g, 1.00 mmol) was dissolved in 10.0 mL acetonitrile dark green colour solution is formed. To this solution ,1,10-phenantroline (0.596 g , 3.00 mmol), dissolved in10.0mL acetonitrile was added and stirring was carried out for 15 min, green colour solution is formed. To this resulting mixture, iodine(0.508g, 2.00 mmol) dissolved in 10.0mL acetonitrile and bromine(0.300 mL, 5.82 mmol) dissolved in 10.0 mL acetonitrile were added and stirring was continued for 10 min. Clear brick red colour solution formedwas filtered and kept for crystallization at 5 °C. The dark green crystals formed were collected after 4 days. Yield: 1.093 g (0.838 mmol,83.8%), Anal.Calc.for $C_{36}H_{24}Br_4CuI_3N_6$(M.W,1304.49): C, 32.06; H, 1.86; N,6.51.Found:C, 1.18;N, 0.77;H,5.28.Important IR absorptions(KBr/cm^{-1}): 2357, 1577, 1515, 1417, 1340, 1216, 1102, 952,833, 771, 715, 637, 508.

2.3 .Physical measurement: IR spectra were recorded by using KBr pellets on a Jasco 5300 FT/IR infrared spectrometer. Elemental analysis for C, H and N was obtained using a FLASH Ea 1112 SERIES CHNS analyser.

2.4 .X-ray Crystallography: X-ray data was collected for complex on a Bruker D8 Quest APEX CCD X-ray diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were reduced using SAINTPLUS[13] and a multi-scan absorption correction using SADABS[14] was performed. The structure was solved using SHELXS-97[15] and full matrix least squares refinement against $F^2$was carried out using SHELXL-97. All ring hydrogens were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms.Crystallographic data and structure refinement parameters are presented in Table1.

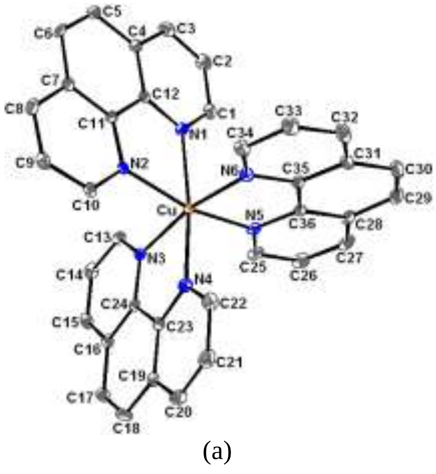
Table 1. Crystallographic data and structure refinement for $[Cu(phen)_3](IBr_2)(I_4Br_4)_{0.5}$.

Formula	$C_{36}H_{24}Br_4CuI_3N_6$
Formula weight	1304.49
Crystal system	Triclinic
a (Å)	12.6650(6)
b (Å)	13.1915(6)
c (Å)	13.4211(6)
α(°)	79.097(2)
β(°)	65.2330(10)
γ(°)	71.301(2)
V(Å^3)	1924.63(16)
Z	2
space group	$P\overline{1}$
T (K)	100(2)
$\rho_{calcd.}$ (g cm^{-3})	2.251
μ (mm^{-1})	7.162
θ Range (°)	2.263 to 27.581
$h/k/l$ indices	–16/16, –17/17, –17/17
Reflections collected	80608
Uniquereflect, R_{int}	8861, 0.0391
GOOF	1.035
$R1[I > 2(\sigma I)]$	0.0658
$wR2$[all data]	0.1474

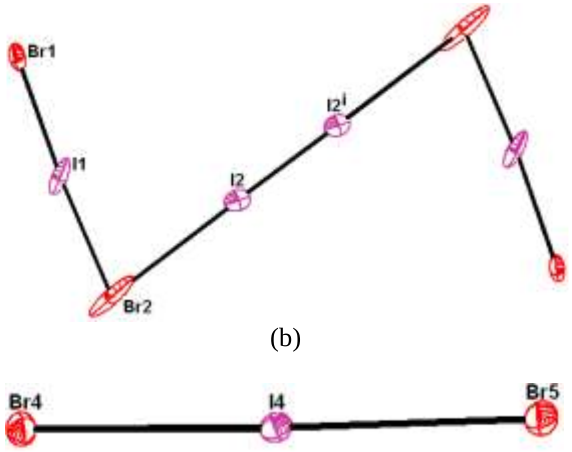
III. Results and Discussion

Compound consisting a$[Cu(phen)_3]^{2+}$tris–chelate cation and $(I_4Br_4)^{2-}{}_{0.5}$, $(IBr_2)^{-}$anions in the asymmetric unit. General views of the ORTEP diagram of cation and anions are shown in Figure1. The complex crystallize in the triclinic system, space group $P\overline{1}$, with two molecules in the unit cell. The average metric parameters (Å, °) for the $Cu(phen)_3^{2+}$ is Cu–N 2.13 Å, N–Cu–N (linear) 169.1°, N–Cu–N (bite) 88.8°. Selected bond lengths and bond angles for compound given in Table 2 and parameters are comparable with previously reported structures.[16] The cation of $[Cu(phen)_3]^{2+}$associated withtwo different type of mixed polyhalide ions, one iscentrosymmetric Z–shape of iodobromide $(I_4Br_4)^{2-}$ and other one is unsymmetrical IBr_2^- anion as shown in Figure 1. The centrosymmetric $(I_4Br_4)^{2-}$may be viewed as two IBr_2^-ions connecting to a central I_2 molecule giving a Z–shape to the ion (Figure 1(b)). In literature Z–shape ions of polyiodides (I_8^{2-}) and polybromides (Br_8^{2-}) are reported in several times, but the mixediodobromides known only one structure with $(I_2Br_6)^{2-}$.[12] Therefore this is the second structure of mixed iodobromide $(I_4Br_4)^{2-}$ Z–shape ion. In contrast to both Z–shape of iodobromide structure, present structure reveals slightly larger bond distances, bond angle of (Br–I–Br) and angle at Z–bend is shorter.

The other one is IBr_2^- ion, which contains unsymmetrical bond distances (2.683 and 2.717 Å) and nearly linear bond angle (178.5°). The tri-iodobromide (IBr_2^-) anions are reported in huge numbers with different organic and inorganic cations.[10] In comparison with reported ions, the bond distances and bond angles are nearly same and no significant differences are observed.



(a)



(b)

(c)

Figure 1. ORTEP view of $[Cu(phen)_3](IBr_2)(I_4Br_4)_{0.5}$. (a) Tris-chelate of $[Cu(phen)_3]^{2+}$, (b) Z–Shape of $(I_4Br_4)^{2-}{}_{0.5}$ and (c) $(IBr_2)^-$ anion.(i= $-x+1,-y+1,-z+1$)

Table 2. Selected bond lengths [Å] and bond angles [°] for $[Cu(phen)_3](IBr_2)(I_4Br_4)_{0.5}$.

Cu-N(1)	2.355(6)	Cu-N(2)	2.074(6)	Cu-N(3)	2.017(6)
Cu-N(4)	2.237(6)	Cu-N(5)	2.061(6)	Cu-N(6)	2.014(6)
Br(1)-I(1)	2.6910(13)	Br(2)-I(1)	2.7866(16)	Br(2)-I(2)	3.387(3)
Br(3)-I(3)	2.7166(8)	Br(4)-I(3)	2.6826(9)	I(2)-I(2)#1	2.6692(13)
N(1)-Cu-N(2)	75.7(2)	N(1)-Cu-N(3)	100.2(2)	N(1)-Cu-N(4)	172.9(2)
N(1)-Cu-N(5)	90.2(2)	N(1)-Cu-N(6)	90.0(2)	N(2)-Cu-N(3)	92.2(2)
N(2)-Cu-N(4)	97.3(2)	N(2)-Cu-N(5)	165.7(2)	N(2)-Cu-N(6)	95.0(2)
N(3)-Cu-N(4)	78.7(2)	N(3)-Cu-N(5)	93.1(2)	N(3)-Cu-N(6)	168.7(2)
N(4)-Cu-N(5)	96.8(2)	N(4)-Cu-N(6)	91.8(2)	N(5)-Cu-N(6)	81.9(2)
Br(1)-I(1)-Br(2)	176.10(7)	Br(2)-I(2)-I(2) #1	172.18(4)	Br(4)-I(3)-Br(3)	178.47(3)
(#1): $-x+1,-y+1,-z+1$					

IV. Conclusion

In this report we presented synthesis of one new complex and their important IR–bands. Crystal structure determination was done for complex .The crystal structure reveals a new centrosymmetric iodobromide $(I_4Br_4)^{2-}{}_{0.5}$ ion.

References

[1] Popov, A. I.; Gutmann, V. *Halogen Chemistry*, Academic Press, London, **1967**, *1*, 225; (b) Down, A. J.; Adams, C. J.; Bailer, J. C.; EmeleÂus, H. J.; Nyholm, R.; Trotman-Dickenson, A.F. *Comprehensive Inorganic Chemistry*, Pergamon, Oxford, **1973**, *3*, 1476; (c) Coppens, P.; Miller, J. S. *Extended Linear Chain Compounds*, Plenum, New York, **1982**, 333.

[2] Svenson, P. H.; Kloo, L. *Chem. Rev.*, **2003**, *103*, 1649.

[3] Blake, A. J.; Devillanova, F. A.; Gould, R. O.; Sheung Li, W.; Lippolis, V.; Parsons, S.; Radek, C.; Schroder, M. *Chem. Soc. Rev.***1998**, *27*, 195.

[4] Haller, H.; Riedel, S. *Z.Anorg. Allg. Chem.*, **2014**, *640*, 1281.

[5] Easton, M. E.; Ward, A. J.; Hudson, T.; Turner, P.; Masters, A. F.; Maschmeyer, T. *Chem. Eur. J.* 2015, *21*, 2961.

[6] Fabjan, C.; Drobits, J. *In Handbook of Battery Materials*;J. O. Ed. Besenhard, Wiley-VCH: Weinheim, Germany, **1999**, 177.

[7] Khan, M. D.; Majibur, R.; Gotoh, Y.; Morikawa, H.; Miura, M. *Textile Res. J.***2009**, *79*, 1305.

[8] K.J. Cathro, K. Cedzynska, D. C. Constable, *J. Power Sources*, **1985**, *16*, 53.

[9] (a) Assouma, C. D.; Crochet, A.; Cheremond, Y.; Giese, B.; Fromm, K. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 4682; (b) Torrent, M. M.; Ribera, E.; Tkacheva, V.; Mata, I.; Molins, E.; Gancedo, J. V.; Khasanov, S.; Zorina, L.; Shibaeva, R.; Wojciechowski, R.; Ulanski, J.; Wurst, K.; Veciana, J.; Laukhin, V.; Canadell, E.; Laukhina, E.; Rovira, C. *Chem. Mater.* **2002**,*14*, 3295; (c) Chernov'yants, M. S.; Burykin, I. V.; Berezov, P. N.; Starikova, Z. A. *Mendeleev Commun*,**2010**, ***20***, 182; (d) Chernovyants, M. S.; Burykin, I. V.; Kostrub, V. V.; Tsupak, E. B.; Starikova Z. A.; Kirsanova, J. A. *J. Mol. Struct.***2012**, *98*, 1010; (e) Ferraro, J. R.; Beno, M. A.; Thorn, R. J.; Wang, H. H.; Webb, K. S.; Williams, J. M. *J. Phys. Chem. Solids*,**1986**, *47*, 301; (f) Dautatel, O. J.; Fourmigue, M.; Canadell, E. *Chem. Eur. J.***2001**, *7*, 2635; (g) Chekhlov, A. N. *J. Struct. Chem.***2007**, *48*, 137; (h) Buist, A. R.; Kennedy, A. R. *Cryst.Growth Des.* **2014**, *14*, 6508; (i) Rujas, J. M.; Meazza, L.; Lim, G. K.; Terraneo, G.; Pilati, T.; Harris, K. D. M.; Metrangolo, P.; Resnati, G. *Angew. Chem. Int. Ed.***2013**, *52*, 13444; (j) Johnson, M. T.; Dzolic, Z.; Cetina, M.; Wendt, O. F.; Ohrstrom, L.; Rissanen, K. *Cryst. Growth Des.* **2012**,*12*, 362; (k) Laukhina,E. E.; Narymbetov,B. Z.; Zorina, L.V.; Khasanov,S. S.; Rozenberg,L. P.; Shibaeva,R. P.; Buravov, L. I.; Yagubskii,E. B.; Avramenko,N. V.; Van,K. *Synth. Met.***1997**,*90*, 101; (l) Tateno, A.; Udagawa, T.; Naito, T.; Kobayashi, H.; Kobayashib, A.; Nogami, T. ***J.** Mat. Chem.* **1994,** *4*, 1559; (m) Emge, V. H.; Wang, H.; Beno, M. A.; Leung, P. C. W.; Firestone, M. A.; Jenkins, H. C.; Cook, J. D.; Carlson, K. D.; Williams, J. M. *Inorg. Chem.***1985**,*24*, 1738; (n) Chaviara, A. T.; T sipis, A. C.; Cox, P. J.; Bolos, C. A. *Eur. J. Inorg. Chem.***2005**, 3491; (o) Baker, P. K.; Drew, M. G. B.; Meehan, M. M. *Inorg. Chem. Commun.***2000**, *3*, 393; (p) Kobayashi, H.; Kato, R.; Kobayashi, A.; Saito, G.; Tokumoto, M.; Anzai, H.; Ishiguro, T. *Chem.Lett.***1985**,1293; (q) Endres, H.; Hiller, M.; Keller, H. J.; Bender, K.; Gogu, E.; Heinen, I.; Schweitzer, D.; *Z.Naturforsch.,B: Chem.Sci.***1985**, *40*, 164; (r) Schultz, A. J.; Emge, T. J.; Leung, P. C.; Beno, M. A.; Wang, H. H.; Williams, J. M. *Physica B and C*, **1986**, *143*, 351; (s) Emge, T. J.; Leung, P. C. W.; Beno, M. A.; Wang, H. H.; Firestone, M. A.; Webb, K. S.;

Carlson, K. D.; Williams, J. M. *Mol.Cryst.Liq.Cryst.***1986**, *132*, 363; (t) Kazheva, O. N.; Aleksandrov, G. G.; Dyachenko, O. A.; Chernovyants, M. S.; Simonyan, S. S.; Lykova, E. O. *Russ.Coord.Chem.* **2003**, *29*, 883; (u) Shilov, G. V.; Kazheva, O. N.; Dyachenko, O. A.; Chernovyants, M. S.; Simonyan, S. S.; Goleva, V. E.; Pyshchev, A. I. *Russ. J. Phys.Chem.***2002**, *76*, 1436.

[10] (a) Maleckis, A.; Kampf, J. W.; Sanford, M. S. *J. Am. Chem. Soc.***2013**, *135*, 6618; (b) Giese, M.; Albrecht, M.; Ivanova, G.; Valkonen, A.; Rissanen, K. *Supramole. Chem.***2012**, *24*, 48; (c) Aragoni, M. C.; Arca, M.; Devillanova, F. A.; Hursthouse, M. B.; Huth, S. L.; Isaia, F.; Lippolis, V.; Mancini, A.; Verani, G. *Eur. J. Inorg. Chem.***2008**, 3921; (d) Janczak, J.; Kubiak, R. *Polyhedron*, **2003**, *22*, 313;(e) Janczak, J.; Perpetuo, G. J. *Polyhedron*, **2006**, *25*, 3319.

[11] Parlow, A.; Hartl, H. *Z. Naturforsch,***1985**, *40b*, 45.

[12] Minkwitz, R.; Berkei, M.; Ludwig, R. *Inorg. Chem.***2001**, *40*, 25.

[13] Babu, R.;Bhargavi, G.;Rajasekharan, M.V.*Eur. J. Inorg. Chem.***2015**, 4689

[14] *SAINTPLUS*, Bruker AXS Inc., Madison, Wisconsin, USA, **2003**.

[15] Sheldrick, G. M. *SADABS*, Program for Empirical Absorption Correction, University of Gottingen, Gottingen, Germany, **1996**.

[16] Sheldrick, G. M. *SHELX-97*, Programs for Crystal Structure Analysis, University of Gottingen, Gottingen, Germany, **1997**.

[17] Babu, R.;Bhargavi, G.;Rajasekharan,M. V. *communicated* to *Inorg. Chimi. Acta*.