Crystal structures of (di-2-pyridyl ketone)zinc dibromide and diiodide, $Zn(C_{11}H_8N_2O)X_2$ (X = Br,I)

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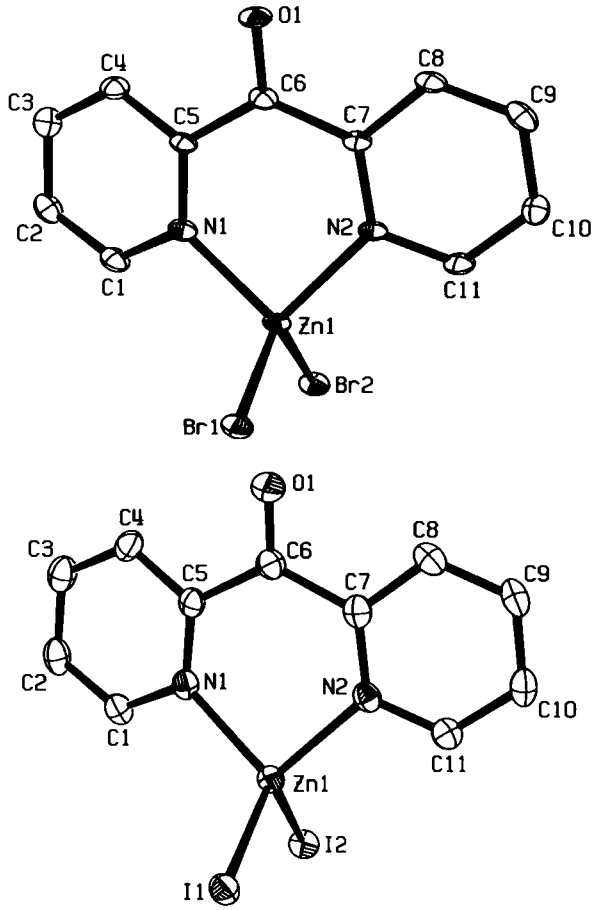
Received June 29, 2004, accepted and available on-line October 6, 2004; CCDC nos. 1267/1360, 1267/1361



Abstracts

$C_{11}H_8Br_2N_2OZn$, monoclinic, $P12_1/c1$ (no. 14), a = 12.300(2) Å, b = 8.070(2) Å, c = 12.751(3) Å, β = 103.229(3)°, V = 1232.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.101, T = 100 K.

$C_{11}H_8I_2N_2OZn$, monoclinic, $P12_1/c1$ (no. 14), a = 12.6266(5) Å, b = 8.3959(3) Å, c = 13.1079(5) Å, β = 103.649(1)°, V = 1350.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.071, T = 100 K.

Source of material

In modification of a previous report [1], di-2-pyridyl ketone (dpk) was reacted separately with zinc bromide (1.35 mmol dpk, 1.42 mmol $ZnBr_2$) and zinc iodide (1.00 mmol dpk, 1.05 mmol ZnI_2) in 40 mL of hot 1-butanol. Upon slow evaporation of the solutions after 12 hours, the $ZnBr_2$ solution produced white crystals of $Zn(dpk)Br_2$ and the ZnI_2 solution produced yellow crystals of $Zn(dpk)I_2$.

Discussion

Both complexes exhibit similar structures with distorted tetrahedral environment of the zinc atom and are isomorphous to a previously reported chloride complex [2]. Differences in the Zn—X (X = Cl, Br, I) bond distances and X–Zn–X angles follow a trend expected from order of size and electronegativity in the periodic table. Chloride, as the smallest ion, exhibits the shortest Zn—Cl distance (2.202 Å vs. 2.356(7) Å for Zn—Br and 2.542(5) Å for Zn—I); conversely, chlorine is the most electronegative of the three elements and thus the Cl–Zn–Cl angle is the largest (118.1° vs. 116.72(2)° for Br–Zn–Br, and 114.86(2)° for I–Zn–I). In the ORTEP drawings at the 50 % probability level (figure) hydrogen atoms have been omitted.

1. (Di-2-pyridyl ketone)zinc dibromide, $Zn(C_{11}H_8N_2O)Br_2$

Table 1. Data collection and handling.

Crystal:	white prism, size 0.05 × 0.14 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	84.61 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX CCD, ω
$2\theta_{max}$:	56.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11266, 3052
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2600
$N(param)_{refined}$:	154
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP-3 [5], SHELXTL-Plus [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.9467	0.5173	0.6846	0.022
H(2A)	4e	1.0333	0.7253	0.6082	0.023
H(3A)	4e	0.9522	0.8148	0.4324	0.025
H(4A)	4e	0.7867	0.6880	0.3379	0.020
H(8A)	4e	0.4552	0.3827	0.3041	0.018
H(9A)	4e	0.3226	0.2239	0.3648	0.022
H(10A)	4e	0.3697	0.1101	0.5385	0.020
H(11A)	4e	0.5474	0.1554	0.6456	0.019

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	0.75870(3)	0.30151(5)	0.64492(3)	0.0147(2)	0.0188(2)	0.0045(2)	0.0003(2)	–0.0022(2)	0.0006(2)
Br(1)	4*e*	0.85243(3)	0.04843(5)	0.64625(3)	0.0168(2)	0.0194(2)	0.0115(2)	0.0018(1)	–0.0003(2)	0.0005(1)
Br(2)	4*e*	0.74673(3)	0.41015(5)	0.81424(3)	0.0217(2)	0.0228(2)	0.0063(2)	0.0012(2)	–0.0000(2)	–0.0022(1)
O(1)	4*e*	0.6288(2)	0.5111(4)	0.3036(2)	0.023(1)	0.026(2)	0.006(1)	–0.003(1)	–0.001(1)	0.002(1)
N(1)	4*e*	0.8173(3)	0.4819(4)	0.5615(3)	0.016(2)	0.017(2)	0.008(2)	–0.000(1)	–0.001(1)	–0.002(1)
N(2)	4*e*	0.6057(3)	0.2919(4)	0.5410(3)	0.016(1)	0.016(2)	0.006(2)	0.001(1)	–0.000(1)	0.000(1)
C(1)	4*e*	0.9134(3)	0.5535(5)	0.6136(3)	0.017(2)	0.023(2)	0.012(2)	0.000(2)	–0.003(2)	–0.002(2)
C(2)	4*e*	0.9658(3)	0.6772(5)	0.5687(3)	0.016(2)	0.020(2)	0.020(2)	–0.001(2)	0.000(2)	–0.006(2)
C(3)	4*e*	0.9181(3)	0.7295(5)	0.4651(3)	0.020(2)	0.021(2)	0.021(2)	–0.001(2)	0.006(2)	–0.001(2)
C(4)	4*e*	0.8198(3)	0.6556(5)	0.4097(3)	0.019(2)	0.021(2)	0.010(2)	0.001(2)	0.002(2)	0.000(2)
C(5)	4*e*	0.7702(3)	0.5343(4)	0.4600(3)	0.014(2)	0.016(2)	0.007(2)	0.002(1)	–0.001(1)	–0.002(1)
C(6)	4*e*	0.6593(3)	0.4662(5)	0.3965(3)	0.016(2)	0.020(2)	0.007(2)	0.002(1)	0.001(1)	–0.002(1)
C(7)	4*e*	0.5787(3)	0.3598(4)	0.4411(3)	0.016(2)	0.015(2)	0.004(2)	0.001(1)	0.001(1)	–0.003(1)
C(8)	4*e*	0.4731(3)	0.3353(5)	0.3741(3)	0.018(2)	0.020(2)	0.006(2)	0.002(2)	–0.000(1)	–0.001(1)
C(9)	4*e*	0.3946(3)	0.2416(5)	0.4099(3)	0.015(2)	0.022(2)	0.015(2)	0.002(2)	–0.001(2)	–0.007(2)
C(10)	4*e*	0.4224(3)	0.1743(5)	0.5120(3)	0.017(2)	0.017(2)	0.016(2)	–0.002(2)	0.006(2)	–0.002(2)
C(11)	4*e*	0.5285(3)	0.2018(5)	0.5753(3)	0.020(2)	0.020(2)	0.007(2)	0.002(2)	0.002(2)	0.002(1)

2. (Di-2-pyridyl ketone)zinc diiodide, $Zn(C_{11}H_8N_2O)I_2$

Table 4. Data collection and handling.

Crystal:	yellow needle, size 0.15 × 0.20 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	63.76 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX CCD, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12773, 3099
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2907
$N(param)_{refined}$:	154
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP-3 [5], SHELXTL-Plus [6]

Table 5. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1B)	4*e*	0.5601	0.5105	0.3250	0.028
H(2B)	4*e*	0.4755	0.7064	0.4016	0.032
H(3B)	4*e*	0.5595	0.7966	0.5715	0.033
H(4B)	4*e*	0.7222	0.6776	0.6607	0.029
H(8B)	4*e*	1.0424	0.3842	0.6919	0.029
H(9B)	4*e*	1.1707	0.2289	0.6320	0.031
H(10B)	4*e*	1.1216	0.1156	0.4638	0.030
H(11B)	4*e*	0.9472	0.1611	0.3603	0.027

Table 6. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	0.74326(3)	0.30451(5)	0.36113(3)	0.0172(2)	0.0199(2)	0.0195(2)	0.0007(1)	0.0028(2)	–0.0005(2)
I(1)	4*e*	0.64318(2)	0.04221(3)	0.35591(2)	0.0185(1)	0.0214(1)	0.0240(1)	–0.00146(8)	0.00408(9)	–0.00020(8)
I(2)	4*e*	0.75137(2)	0.41533(3)	0.18184(2)	0.0257(1)	0.0229(1)	0.0211(1)	–0.00110(9)	0.0055(1)	0.00248(8)
O(1)	4*e*	0.8764(2)	0.5076(4)	0.6932(2)	0.026(1)	0.034(2)	0.023(1)	0.003(1)	0.002(1)	–0.004(1)
N(1)	4*e*	0.6881(2)	0.4783(3)	0.4438(2)	0.018(1)	0.016(1)	0.026(2)	0.001(1)	0.006(1)	0.002(1)
N(2)	4*e*	0.8935(2)	0.2946(3)	0.4618(2)	0.017(1)	0.018(1)	0.024(2)	–0.002(1)	0.003(1)	0.002(1)
C(1)	4*e*	0.5935(3)	0.5453(4)	0.3941(3)	0.019(2)	0.024(2)	0.027(2)	–0.000(1)	0.003(2)	0.001(1)
C(2)	4*e*	0.5428(3)	0.6623(5)	0.4388(3)	0.020(2)	0.022(2)	0.039(2)	0.004(1)	0.008(2)	0.007(2)
C(3)	4*e*	0.5919(3)	0.7145(5)	0.5392(3)	0.027(2)	0.021(2)	0.039(2)	0.001(1)	0.015(2)	0.001(2)
C(4)	4*e*	0.6881(3)	0.6454(5)	0.5912(3)	0.025(2)	0.023(2)	0.028(2)	–0.002(1)	0.013(2)	–0.004(1)
C(5)	4*e*	0.7356(3)	0.5278(4)	0.5415(3)	0.017(2)	0.018(2)	0.023(2)	–0.003(1)	0.008(1)	0.001(1)
C(6)	4*e*	0.8448(3)	0.4643(4)	0.6030(3)	0.019(2)	0.021(2)	0.022(2)	–0.001(1)	0.005(1)	0.001(1)
C(7)	4*e*	0.9212(3)	0.3598(4)	0.5588(3)	0.018(2)	0.017(2)	0.026(2)	–0.002(1)	0.008(1)	0.004(1)
C(8)	4*e*	1.0240(3)	0.3374(5)	0.6240(3)	0.019(2)	0.029(2)	0.023(2)	–0.004(1)	0.002(1)	0.003(2)
C(9)	4*e*	1.1000(3)	0.2455(5)	0.5886(3)	0.015(2)	0.032(2)	0.029(2)	0.002(1)	0.003(1)	0.007(2)
C(10)	4*e*	1.0713(3)	0.1789(5)	0.4896(3)	0.018(2)	0.023(2)	0.036(2)	0.003(1)	0.010(2)	0.004(2)
C(11)	4*e*	0.9671(3)	0.2065(4)	0.4286(3)	0.021(2)	0.023(2)	0.023(2)	–0.001(1)	0.005(1)	0.001(1)

Acknowledgments. GC and BLW were supported by CSU-AAUP Faculty Research Grants. ADH, MZ, and JU were supported by NSF grant 0111511, and the diffractometer was funded by NSF grant 0087210, by Ohio Board of Regents grant CAP-491, and by YSU.

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