Monatshefte für Chemie 112, 529—532 (1981)

Monatshefte für Chemie

Correlation of Colour and Crystal Structure for Silver(I) Compounds

Short Communication

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(Received 15 January 1981. Accepted 23 January 1981)

A geometrical analysis on 22 crystal structures of Ag(I) compounds with "hard" bases demonstrates that the observed colour-changes from colourless to red depend on the number of Ag(I) atoms coordinating the donor atoms of the base.

[Keywords: Colour of silver(I)compounds; Crystal structures of silver(I) compounds]

Korrelation zwischen Farbe und Kristallstruktur in Silber(I)-Verbindungen (Kurze Mitteilung)

Eine geometrische Analyse an 22 Kristallstrukturen von Ag(I)-Verbindungen mit „harten" Basen zeigt, daß sich die Farbe der Verbindungen mit steigender Anzahl von Silberatomen um die Donorzentren vertieft.

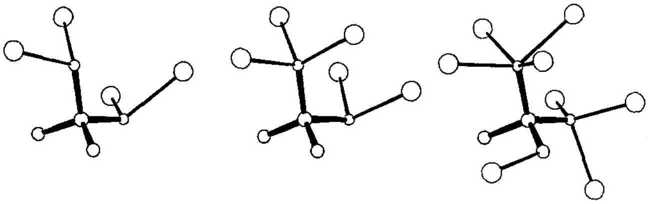
Occasionally, silver(I) is observed to form red or yellow crystalline compounds with colourless anions. The appearance of colour in such crystals does not seem to depend solely on the chemical identity of the anion; for example, Ag(I) sulfamides show different colours, depending on the stoichiometry: Disilversulfamide crystals (Ag 2 *SA*) are colourless, Trisilversulfamide crystals (Ag 3 *SA*) are yellow and Tetrasilversulfamide crystals (Ag 4 *SA*) are deep red[1–3].

The phenomenon of colour in silver(I) compounds was interpreted in terms of the concept of *Pitzer* and *Hildebrand*[4], which postulates that the depth of the colour should increase with the covalent character of

0026-9247/81/0112/0529/$ 01.00

the metal-anion bonds in question. On this basis, the colour was occasionally correlated with the crystallographically observed silver-anion bondlengths[5].

The crystal structures of the three above silver(I)-sulfamides were recently determined[1–3]. They clearly demonstrate, that the colour cannot be explained in terms of the observed Ag—N bondlengths alone, since all three crystal structures show covalent Ag—N bonding distances which differ only immaterially between the three structures (Table 1). The most conspicuous difference between the three crystal structures, however, is the *number* of silver atoms bonded to either of the two sulfamide nitrogen atoms: this coordination number is 2 and 2 in Ag2*SA*, 2 and 3 in Ag3*SA* and 3 and 4 in Ag4*SA*. Fig. 1 shows computer drawings of the sulfamide molecules with all the covalently bonded neighbours, as observed in the three crystal structures.



Ag2SA **Ag3SA** **Ag4SA**

Fig. 1. Crystal structure of Ag(I) sulfamides. Circles represent, with increasing radii, N,O,S,Ag respectively

We have surveyed the literature for X-ray structure determinations on analogous Ag(I) compounds with hard anions (*Pearson*[6]) in order to see if a similar correlation between colour and Ag-coordination around the (hard) donor atoms *X* (N or O) can be found. From all the structures which came to our attention, we have neglected those which we considered crystallographically questionable or which contained coloured anions (e.g. MnO_4^-, CrO_4^{2-} etc.). The result of a geometrical analysis of the crystal structures of 12 colourless, 2 yellow and 8 red Ag(I) compounds (summerized in Table 1) supports the following statements:

(1) Covalent Ag(I)—*X* bonds are necessary, but not sufficient for the appearance of colour. Thus, all ionic crystals (as judged from the Ag—*X* bondlength and from the coordination number around Ag) are

colourless. However, it is not possible to find a correlation between the length of the Ag—X bond and the colour.

(2) Coloured compounds have systematically higher crystal densities than colourless compounds.

Table 1. *Geometrical analysis of 22 crystal structures of Ag(I) compounds*

Compound	Ref.	Ag—X[a]	Ag—Ag[b]	Z[c]	Density[d]	Colour
Ag_2ClNO_3	7	>2.5	>3.2	1,1,1	4.9	colourless
$AgClO_3$	8	2.5	>3.2	2,2	4.4	
$AgNO_3$	9	2.5	>3.2	2,1,1	4.35	
$Ag(CH_3SO_3)$	10	2.34	3.17	1,1,1	3.3	
$Ag_3(NSO_2)_3 \cdot 3H_2O$	11	2.32	3.033	1,1	3.8	
$AgNO_3$Glyc.	12	2.20	2.87	2,1	2.8	
$AgNCO$	13	2.12	3.19	2	4.2	
$Ag_2H_2N_2O_2S$	1	2.12	3.088	2,2	4.5	
$AgKO$	14	2.10	2.91	2	4.0	
$AgKCO_3$	15	2.09	3.0	1	3.8	
$AgNa_3O_2$	16	2.08	2.96	1	3.95	
$AgNO_3Hg(CN)_2 \cdot (H_2O)_2$	17	2.03	3.20	1,1,1	3.5	
Ag_2CO_3	18	2.23	2.87	2,2	6.07	yellow
$Ag_3HN_2O_2S \cdot NH_3 \cdot H_2O$	2	2.08	2.91	3,2	4.01	
Ag_3NSeO_3	19	2.18	3.05	3	6.6	red
$Ag_6Si_2O_7$	20	2.18	2.95	3,3,(3)	6.6	
$Ag_6(SO_4)(SiO_4)$	21	2.18	2.92	3,(3)	6.3	
Ag_3LiO_2	22	2.15	2.85	3	7.1	
$Ag_4N_2O_2S$	3	2.13	2.87	4,3,1	6.5	
Ag_3NaO_2	23	2.10	2.98	3	6.3	
Ag_6SrO_4	24	2.06	2.81	3,3	7.4	
Ag_6BaO_4	25	2.04	2.83	3,3	7.4	

[a] Shortest Ag—X distance (Å), (X = N or O).
[b] Shortest Ag—Ag distance (Å).
[c] Coordination numbers of Ag(I) around X.
[d] Calculated crystal density (g cm^{-3}).

(3) It is not possible to correlate the colour with the appearance of short Ag—Ag contacts ("Ag-clusters"): There are several examples of colourless compounds with Ag—Ag contact distances of the magnitude observed in metallic silver (2.88 Å).

(4) There is a notable correlation of the observed crystal colour with the number of Ag(I) atoms bonded to any of the donor atoms X (N or O): colourless compounds have coordination numbers (Z) of 1 or 2, whereas red compounds always show coordination numbers of 3 or even 4.

Acknowledgements

Supported by the *Österreichischer Fonds zur Förderung der Wissenschaftlichen Forschung* (*C. K.*, Projekt 3763) and the *Österreichische Akademie der Wissenschaften.*

References

1 *Greschonig, H.*, *Nachbaur, E.*, *Krischner, H.*, Acta Cryst. **B 33**, 3595 (1977).
2 *Kratky, C.*, *Nachbaur, E.*, *Popitsch, A.*, Acta Cryst., in press.
3 *Kratky, C.*, *Popitsch, A.*, Acta Cryst. **B 36**, 1044 (1980).
4 *Pitzer, K. S.*, *Hildebrand, J. H.*, J. Amer. Chem. Soc. **63**, 2472 (1941).
5 *Donohue, J.*, *Helmholz, L.*, J. Amer. Chem. Soc. **66**, 295 (1944); *Palmer, N. G.*, Experimental Inorganic Chemistry. Cambridge: Univ. Press. 1965; *Trotman-Dickenson, A. F.*, Comprehensive Inorganic Chemistry, Vol. III. Oxford: Pergamon Press. 1973.
6 *Pearson, R. G.*, Hard and Soft Acids and Bases. Dowden, Hutchinson and Ross. 1973.
7 *Persson, K.*, Acta Cryst. **B 35**, 1432 (1979).
8 *Naray-Szabo, St. v.*, *Pocza, J.*, Z. Krist. **104**, 28 (1941).
9 *Lindley, P. F.*, *Woodward, P.*, J. Chem. Soc. (A) **1966**, 123.
10 *Charbonnier, F.*, *Faure, R.*, *Loiseleur, H.*, Acta Cryst. **B 33**, 2824 (1977).
11 *Dalgaard, G. A. P.*, *Hazell, A. C.*, *Hazell, R. G.*, Acta Cryst. **B 30**, 2721 (1974).
12 *Mohana Rao, J. K.*, *Viswamitra, M. A.*, Acta Cryst. **B 28**, 1484 (1972).
13 *Britton, D.*, *Dunitz, J. D.*, Acta Cryst. **18**, 424 (1965).
14 *Sabrowsky, H.*, *Hoppe, R.*, Z. anorg. allg. Chem. **358**, 241 (1968).
15 *Barclay, G. A.*, *Hoskins, B. F.*, J. Chem. Soc. **1963**, 2807.
16 *Schenk, F.*, *Hoppe, R.*, Naturwissenschaften **56**, 414 (1969).
17 *Mahon, C.*, *Britton, D.*, Inorg. Chem. **10**, 586 (1971).
18 *Masse, P.*, *Guitel, J. C.*, *Durif, A.*, Acta Cryst. **B 35**, 1428 (1979).
19 *Fawcett, J. K.*, *Kocman, V.*, *Nyburg, S. C.*, *O'Brien, R. J.*, Chem. Comm. **1969**, 1198.
20 *Jansen, M.*, Acta Cryst. **B 33**, 3584 (1977).
21 *Keller, H. L.*, *Müller-Buschbaum, H.*, Z. anorg. allg. Chem. **408**, 205 (1974).
22 *Jansen, M.*, Z. Naturforsch. **B 30**, 854 (1975).
23 *Jansen, M.*, Z. Naturforsch. **B 31**, 1544 (1976).
24 *Keller, H. L.*, *Müller-Buschbaum, H.*, Z. anorg. allg. Chem. **393**, 266 (1972).
25 *Keller, H. L.*, *Müller-Buschbaum, H.*, Z. Naturforsch. **B 28**, 263 (1973).