Inorganica Chimica Acta, 26 (1978) 103–106
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Some Complexes of s-Triazine with Cobalt(II) Halides

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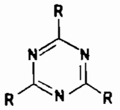
Received May 24, 1977

The isolation of eight new complexes of bivalent cobalt with s-triazine of general formula $CoX_2(trz)_n(H_2O)_m$ *(where* $X = Cl, n = 1, m = 1$ *or* $3; n = 2, m = 1; X = Br, n = 1, m = 0; n = 2, m = 0$ *or* $2; X = I, n = 2, m = 0; X = NCS, n = 4, m = 1$*) is reported. The proposed four- and six-coordinate stereochemistries of these products are assigned after consideration of microanalyses, visible absorption spectra and magnetic moment data. In the main the complexes are stable only in the solid state below room temperature and in the absence of moisture. There is some evidence for a strong interaction between water and s-triazine in the Cl and NCS compounds.*

Introduction

There are many examples reported of the coordination to transition metals of aromatic nitrogeneous bases. Within this class considerable study has been made of the six-membered monocyclic pyridines, pyrimidines and pyrazines. However, possibly both because of its hydrolytic instability [1] and low base strength [2], the molecule s-triazine (trz), (I), does not appear to have received attention from the coordination chemist.



(I) (trz); R = H
(II) (tpt); R = (2′-pyridyl)

In recent years we have prepared and studied a number of metal chelates of the multifunctional substituted-triazine ligand 2,4,6-tris(2′-pyridyl)-s-triazine, (tpt) (II), including those formed with bivalent nickel [3, 4], bivalent cobalt [5, 6] and the lanthanide elements [7]. From studies on this ligand the very low basic properties of the central s-triazine residue became apparent, evidenced both by an inability to protonate in strong acid [3, 4, 8] and to coordinate to a second metal atom once tridentate function had been achieved [9]. More recently it has been noticed

TABLE I. Properties of Cobalt(II) Halide Complexes of s-Triazine.

Compound	Colour	Vis. Abs. (nm)	Mag. Mom. (B.M.)	Proposed Structure
$CoCl_2(trz)_2 \cdot H_2O$	Pale Pink	540	–	Octahedral Polymer
$CoCl_2trz \cdot H_2O$	Pale Green	660	4.69	Tetrahedral Dimer
$CoCl_2(H_2O)_2trz \cdot H_2O$	Pale Grey	554	4.94	Octahedral Dimer
$CoBr_2(trz)_2$	Blue	660	4.71	Tetrahedral Monomer
$CoBr_2trz$	Green	685	4.60	Tetrahedral Dimer
$CoBr_2(H_2O)_2(trz)_2$	Pink	545	5.06	Octahedral Monomer
$CoI_2(trz)_2$	Dark Green	698	4.46	Tetrahedral Monomer
$Co(NCS)_2(trz)_4 \cdot H_2O$	Salmon Pink	460, 555	5.00	Octahedral Monomer

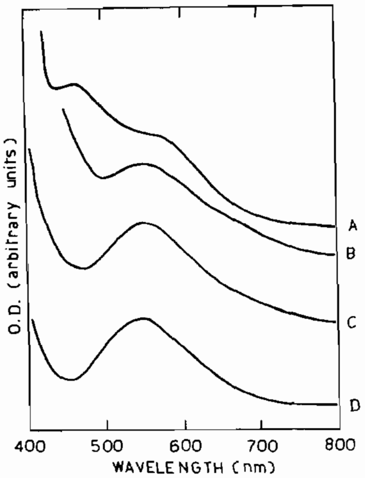


Figure 1. Diffuse reflectance spectra of octahedral cobalt(II) complexes of s-Triazine. A, $Co(NCS)_2(trz)_4 \cdot H_2O$: B, $CoCl_2(H_2O)_2trz \cdot H_2O$; C, $CoCl_2(trz)_2 \cdot H_2O$; D, $CoBr_2(H_2O)_2(trz)_2$.

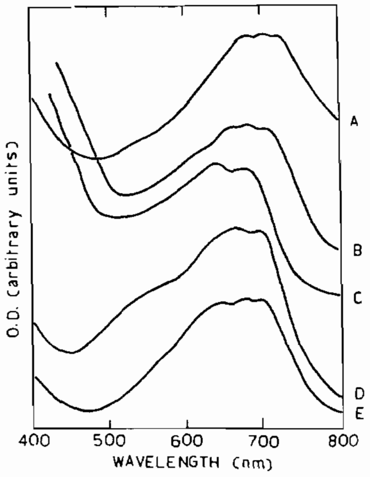


Figure 2. Diffuse reflectance spectra of tetrahedral cobalt(II) complexes of s-Triazine. A, $CoI_2(trz)_2$; B, $CoBr_2trz$; C, $CoCl_2trz \cdot H_2O$; D, $CoBr_2(trz)_2$; E, $CoBr_2py$.

that the ligand tpt also is susceptible to hydrolytic attack at the triazine centre [10].

Our interest in the donor properties of the parent compound s-triazine led to an investigation involving the preparation and characterisation of some compounds of s-triazine formed with cobalt(II) halides. This paper reports the results of that investigation.

Results and Discussion

A number of cobalt(II) complexes of s-triazine were prepared of general formula $CoX_2(trz)_n$ (where X is either Cl, Br, I or NCS and n is 1, 2 or 4) in hydrated or anhydrous forms. In some cases the products proved to be very hygroscopic preventing the isolation of anhydrous forms, although as close to anhydrous conditions as possible were employed. The colour, magnetic moment, visible reflectance data and assigned stereochemistry of each compound based on this data is presented in Table I.

The diffuse reflectance spectra of the complexes are shown in Figures 1 and 2.

The compounds are in general rather unstable particularly in the presence of moisture. They dissolve only in donor solvents such as acetone, nitrobenzene and dimethylformamide and always with displacement of the ligand. Studies were restricted therefore to the solid state. Whenever comparison with equivalent compounds formed by other heterocyclic bases was possible it was found that generally for the triazine compounds the magnetic moments were higher and the visible absorption occurred at higher wavelengths. This is consistent with a weaker ligand field.

Dichlorobis(s-triazine)cobalt(II) monohydrate is a pale pink complex stable below 0 °C in the absence of moisture. At room temperature and under anhydrous conditions this complex loses s-triazine to form the green dichloro(s-triazine)cobalt(II) monohydrate compound. The complex has a reflectance spectrum characteristic of octahedral cobalt(II) and therefore probably possesses a halide-bridged polymeric structure of the kind reported by Gill *et al.* [11] for pyridine complexes of cobalt(II) chloride and thiocyanate where the molecules of the base are *trans* to each other. Reliable magnetic moment data were not obtained because the compound was too difficult to handle.

Attempts to prepare an anhydrous compound of this stoichiometry failed. Microanalyses and infra-red spectra (strong absorption around 3200 cm^{-1}) always indicated the presence of a water molecule, which could not be removed without complete decomposition of the complex. It is possible that the water molecule may add to the complex after product isolation, with no apparent change in the metal's coordination sphere.

The green dichloro(s-triazine)cobalt(II)monohydrate compound may be prepared only by the removal of triazine from the bis complex. Magnetic and spectral data are consistent with tetrahedral cobalt(II) and it is concluded that this substance exists in the form of tetrahedral halide-bridged dimers with the water molecule still uncoordinated. In contrast with the bis complex it is quite stable at room temperature in the absence of moisture. If allowed to stand in air the complex adds on two further water molecules quite readily to form the relatively stable trihydrate $CoCl_2(H_2O)_2trz \cdot H_2O$. This compound subsequently decomposes, as do all of these complexes if exposed to moist air for prolonged periods, probably in part due to the hydrolytic decomposition of s-triazine itself [1]. It is evidently an octahedral complex with the two additional water molecules involved in coordination. Further evidence for this is the fact that this trihydrate compound on heating to 100 °C loses two water molecules and reverts to the green monohydrate form.

A compound of apparent formulation $CoBr_2(trz)_2$ was prepared by direct reaction between cobalt bromide and s-triazine in the appropriate molar ratios. This blue compound is evidently one of the many examples of tetrahedral cobalt monomers formed by heterocyclic monodentates. Upon heating to about 150 °C the compound loses triazine to form the green dibromo(s-triazine)cobalt(II). This latter compound is particularly stable in the absence of moisture. Spectral and magnetic data are consistent with tetrahedral coordination, perhaps achieved by dimerization in a manner similar to that suggested above for the analogous chloro complex. By way of comparison a corresponding green $CoBr_2py$ compound was formed by heating the known blue $CoBr_2py_2$. The visible spectrum (Fig. 2) and magnetic moment (4.63 B.M.) were virtually identical to that of the s-triazine complex.

The pink dibromodiaquobis(s-triazine)cobalt(II) compound is formed by addition of water to the blue tetrahedral species. It is readily reconverted to the blue compound by gentle heating. The structural arrangement presumably involves both of these additional water molecules as part of an octahedral environment around the cobalt atom.

The dark green diiodobis(s-triazine)cobalt(II) compound was prepared by reacting cobalt bromide with the ligand and sodium iodide in ethanol. It is evidently a tetrahedral complex and is stable in the absence of moisture. It decomposes completely on heating.

As is not uncommon the most stable complex formed was the thiocyanate complex $Co(NCS)_2(trz)_4 \cdot H_2O$. Salmon pink in colour, it is stable even in the presence of moist air and the only example of a complex of s-triazine where the coordination sphere includes four molecules of the base. It is assumed that the water molecule is not coordinated since it cannot be removed without simultaneous loss of s-triazine.

It is of interest that, as with the chloro compounds, once again a water molecule is associated with the complex. Lever *et al.* [12] in discussing a similar compound formed with methylpyrazine considered the possibility of seven-coordination. However, since the spectrum and magnetic moment is readily explicable in terms of octahedral symmetry this proposition was rejected in favour of the proposal that the water molecule is held to the base by strong hydrogen bonds. More recent work by Gillard *et al.* [13] has shown that coordinated N-heterocycles may undergo an addition reaction with water molecules across the C–N bond to form "covalent hydrate" species. It is possible that such a species exists in these chelates. The high sensitivity of s-triazine towards attack by water [1], the observed hydrolytic cleavage of part of the central triazine residue of substituted s-triazine-metal complexes [10], and the known formation of a "covalent hydrate" of s-triazine in sulphuric acid solutions [14] would each support such a view.

The ready loss of s-triazine from some of the compounds on standing is in agreement with the low donor properties of the base [2].

Experimental

Synthesis of Compounds

s-Triazine (trz)

Tris(formamine)methane was prepared in 17% yield (m.p. 164 °C; ref. [15] m.p. 164 °C) and this compound pyrolysed to give s-triazine in 61% yield (m.p. 82 °C; ref. [1] m.p. 86 °C), both according to the methods described by Bredereck *et al.* [15].

Dichlorobis(s-triazine)cobalt(II) monohydrate, $CoCl_2(trz)_2 \cdot H_2O$

Anhydrous cobalt chloride (1.3 g) was added to dried absolute ethanol (25 ml) and to this solution was added dropwise a solution of s-triazine (1.6 g) in ethanol. Immediately a fine pink crystalline precipitate formed, which was filtered off and washed with a small volume of ethanol and ether, the solvent was removed by suction, and the solid transferred to a refrigerator. *Anal.* Found: C, 23.6; H, 3.3; Co, 19.2%. $C_6H_8N_6OCl_2Co$ requires: C, 23.2; H, 2.6; Co, 19.0%.

Dichloro(s-triazine)cobalt(II) monohydrate, $CoCl_2trz \cdot H_2O$

A sample of dichlorobis(s-triazine)cobalt(II) monohydrate was allowed to stand for 24 hours in a drybox at room temperature. The pale green finely divided crystalline complex formed was stored in the drybox in a stoppered container. *Anal.* Found: C, 16.1; H, 2.5; N, 16.6; Co, 25.6%. $C_3H_5N_3OCl_2Co$ requires: C, 15.7; H, 2.2; N, 18.4; Co, 25.7%.

This complex also was prepared by heating the bis(s-triazine) complex to 110 °C for 1 hour. The green complex was then transferred to the drybox. *Anal.* Found: C, 16.0; H, 2.4; N, 17.7; Co, 25.3%.

Dichlorodiaquo(s-triazine)cobalt(II) monohydrate, $CoCl_2(H_2O)_2trz \cdot H_2O$

Dichloro(s-triazine)cobalt(II) monohydrate was allowed to stand in the open air for 30 minutes. The grey powder formed was washed with cyclohexane before storage in a closed container in the drybox.

Anal. Found: C, 13.4; H, 3.4; N, 15.6; Co, 22.1%. $C_3H_9N_3O_3Cl_2Co$ requires: C, 13.6; H, 3.4; N, 15.9; Co, 22.2%.

Dibromobis(s-triazine)cobalt(II), $CoBr_2(trz)_2$

Anhydrous cobalt bromide (1.1 g) was dissolved in absolute ethanol (25 ml). To this was added a solution of s-triazine (0.8 g) in ethanol and the mixture thoroughly stirred and set aside to stand for 15 minutes. The blue crystalline product was filtered off, washed with the mother liquor and ether, dried by suction and stored in the drybox. *Anal.* Found: Co, 15.3%, $C_6H_6N_6Br_2Co$ requires: Co, 15.5%.

Dibromo(s-triazine)cobalt(II), $CoBr_2trz$

A small amount of dibromobis(s-triazine)cobalt(II) was heated to 150 °C for two hours. The deep green crystalline product was stored in the drybox.

The complex could be prepared also in very low yield by adding a small amount of anhydrous cobalt bromide dissolved in dried absolute ethanol to a dilute solution of s-triazine in the alcohol. After standing for 30 minutes the deep green compound was filtered off, washed with the mother liquor and ether and dried by suction before storage in the drybox. *Anal.* Found: C, 11.6; H, 2.4; N, 11.5; Co, 19.3%. $C_3H_3N_3Br_2Co$ requires: C, 12.0; H, 1.0; N, 14.0; Co, 19.7%.

Dibromodiaquobis(s-triazine)cobalt(II), $CoBr_2(H_2O)_2(trz)_2$

A small amount of dibromobis(s-triazine)cobalt(II) was allowed to stand in the open for 30 minutes. The pink complex thus formed was washed with cyclohexane and dried by suction. *Anal.* Found: C, 17.4; H, 2.4; N, 20.0; Co, 14.0%. $C_6H_{10}N_6O_2Br_2Co$ requires: C, 17.3; H, 2.4; N, 20.2; Co, 14.1%.

Diiodobis(s-triazine)cobalt(II), $CoI_2(trz)_2$

To a solution of s-triazine (0.8 g) and sodium iodide (0.9 g) in dried ethanol was added anhydrous cobalt bromide (1.1 g) in the ethanol solvent. The mixture was thoroughly stirred and allowed to stand for 30 minutes. The dark green crystalline precipitate which formed was filtered off, washed with the mother liquor, dried ethanol and ether and dried by suction. *Anal.* Found: C, 15.4; H, 2.7; N, 15.1; Co, 12.4%. $C_6H_6N_6I_2Co$ requires: C, 15.2; H, 1.3; N, 17.7; Co, 12.4%.

Diisothiocyanatotetrakis(s-triazine)cobalt(II) monohydrate, $Co(NCS)_2(trz)_4\cdot H_2O$

Anhydrous cobalt thiocyanate (0.45 g) was dissolved in a minimum volume of absolute ethanol. To this solution was added an absolute ethanol solution of s-triazine (0.8 g) and the mixture thoroughly stirred. On standing a salmon pink crystalline complex precipitated. This was filtered off, washed with mother liquor, ethanol and ether and the solvent removed by suction. *Anal.* Found: C, 32.4; H, 2.7; N, 38.2; Co, 11.5%. $C_{14}H_{14}N_{14}OS_2Co$ requires: C, 32.5; H, 2.7; N, 37.9; Co, 11.4%.

Dibromo(pyridine)cobalt(II), $CoBr_2py$

A small amount of highly crystalline dibromobis(pyridine)cobalt(II) was heated at 180 °C for 5 hours. A green complex remained, which was immediately transferred to a drybox. *Anal.* Found: Co, 20.0%. $C_5H_5NBr_2Co$ requires: Co, 19.8%.

Analytical Methods

Cobalt was determined volumetrically as the pyridine–thiocyanate complex [16]. Carbon, hydrogen and nitrogen were determined by Dr. E. Challen at the University of New South Wales. Some difficulty was encountered in analysing for H and N with the more unstable or hygroscopic complexes. These values are included when determined although their accuracy is doubtful. Particular care was taken in the determination of % metal composition. Nonetheless the formulations $CoBr_2(trz)_2$, $CoBr_2trz$ and $CoI_2(trz)_2$ could be considered as doubtful.

References

1 C. Grundmann and A. Kreutzberger, *J. Am. Chem. Soc., 76,* 632 (1954).
2 R. D. Johnston, R. S. Vagg and E. C. Watton, *Inorg. Chim. Acta, 22,* L37 (1977).
3 R. S. Vagg, R. N. Warrener and E. C. Watton, *Aust. J. Chem., 20,* 1841 (1967).
4 G. A. Barclay, R. S. Vagg and E. C. Watton, *Aust. J. Chem., 22,* 643 (1969).
5 R. S. Vagg, R. N. Warrener and E. C. Watton, *Aust. J. Chem., 22,* 141 (1969).
6 H. A. Goodwin, R. N. Sylva, R. S. Vagg and E. C. Watton, *Aust. J. Chem., 22,* 1605 (1969).
7 J. V. Kingston, E. M. Krankovits, R. J. Magee, E. C. Watton and R. S. Vagg, *Inorg. Nucl. Chem. Lett., 5,* 445 (1969).
8 P. F. Collins, H. Diehl and G. F. Smith, *Analyt. Chem., 31,* 1862 (1959).
9 G. A. Barclay, R. S. Vagg, R. N. Warrener and E. C. Watton, *Proc. XII Internat. Conf. Coord. Chem., Sydney,* 177 (1969).
10 E. I. Lerner and S. J. Lippard, *J. Am. Chem. Soc., 98,* 5397 (1976).
11 N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie and P. J. Pauling, *J. Inorg. Nucl. Chem., 18,* 88 (1961).
12 A. B. P. Lever, J, Lewis and R. S. Nyholm, *J. Chem. Soc.,* 5042 (1963).
13 (a) R. D. Gillard, *Coord. Chem. Rev., 16,* 67 (1975).
(b) R. D. Gillard, C. T. Hughes and P. A. Williams, *Trans. Met. Chem., 1,* 51 (1976).
14 B. A. Korolev, M. A. Mal'tseva and N. A. Andronova, *Zh. Obshch. Khim., 45,* 234 (1975).
15 H. Bredereck, R. Gompper, H. Rempfer, K. Klemm and H. Keck, *Chem. Ber., 92,* 329 (1959); *96,* 3260 (1963).
16 A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis", Longman, London, 3rd Ed., p. 268 (1961).