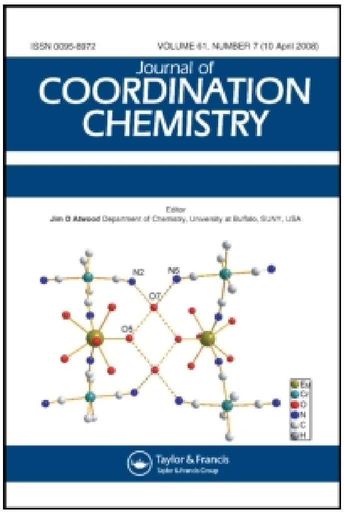

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THE CRYSTAL STRUCTURES OF [(4-MepyO)$_2$H](I$^-_3$) AND [Co(4-EtO$_2$CpyO)$_6$](I$^{2-}_8$), PRODUCTS OF AEROBIC DECOMPOSITION FROM ETHANOLIC SOLUTIONS OF SO$_2$ ADDUCTS CONTAINING PYRIDINE-*N*-OXIDE DERIVATIVES

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THE CRYSTAL STRUCTURES OF $[(4\text{-MepyO})_2\text{H}](\text{I}_3^-)$ AND $[\text{Co}(4\text{-EtO}_2\text{CpyO})_6](\text{I}_8^{2-})$, PRODUCTS OF AEROBIC DECOMPOSITION FROM ETHANOLIC SOLUTIONS OF SO_2 ADDUCTS CONTAINING PYRIDINE-*N*-OXIDE DERIVATIVES

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Four samples of SO_2 adducts in ethanol or toluene solutions, $CuCl_2(2,6\text{-MepyO})_2(SO_2)_{0.5}(H_2O)_2$, $CuBr_2(3\text{-HOH}_2\text{CpyO})_2(SO_2)_{0.5}$, $MnI_2(4\text{-MepyO})_2(SO_2)_{0.75}(H_2O)_4$ and $CoI_2(4\text{-CNpyO})_2(SO_2)_{0.75}(H_2O)_2$, were exposed to air at room temperature by simply exposing them to air for about a month or by bubbling air into the solution for 4 h and subsequent stirring for 12 h. After this procedure, oxidation products and ligand derivatives, obtained from adducts where SO_2 bridged between two metal centres, were isolated and characterised. Thus, the aerobic oxidation of $MnI_2(4\text{-MepyO})_2(SO_2)_{0.75}(H_2O)_4$ and $CoI_2(4\text{-CNpyO})_2(SO_2)_{0.75}(H_2O)_2$, respectively, yield the decomposition products $[(4\text{-MepyO})_2H](I_3)$ and $[Co(4\text{-EtO}_2\text{CpyO})_6](I_8)$, which have been crystallographically characterised. Furthermore, we have isolated and clearly identified blue crystals of $CuSO_4 \cdot 5H_2O$ from solutions of both $CuCl_2(2,6\text{-MepyO})_2(SO_2)_{0.5}(H_2O)_2$ and $CuBr_2(3\text{-HO}_2\text{HCpyO})_2(SO_2)_{0.5}$.

Keywords: Sulfur dioxide; pyridine-*N*-oxide; crystal structure; aerobic decomposition; adducts; cobalt

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INTRODUCTION

Earlier work[1–4] on heavy transition metal compounds has shown that stable SO_2 adducts could be formed. Our interest in the binding of sulfur dioxide to transition metal complexes is derived, firstly, from the aim to develop a system for reversibly coordinating this insidious air pollutant. Systems which allow reversible coordination might eventually lead to the development of a scrubbing system for removal of sulfur dioxide from flue gas stacks. Our own endeavours have been directed to systems which engage sulfur dioxide so that a labile linkage is formed and we have been able to do this with first-row transition metal complexes. For some time we have been investigating the binding of sulfur dioxide by complexes of the first-row transition metals[5–8] and we have demonstrated reversible binding of sulfur dioxide in a series of manganese(II), iron(II), cobalt(II) and copper(II) species containing mainly oxygen-donor neutral ligands, such as tertiary phosphine oxides, tertiary arsine oxides or pyridine-*N*-oxides.

A further interest has been raised by our observations that, in certain cases, the coordinated sulfur dioxide is activated and, when exposed to moist air, and in the presence of an excess of the ancillary ligand, can produce derivatives of ligands and sulfuric acid[9] such as $(Ph_3PO)(Ph_3POH)HSO_4$, and $(Ph_3AsOH)HSO_4$. There is clearly some extremely interesting redox chemistry in these systems, so the investigation of this phenomenon has become another aim of our research. We have been able to observe some fascinating redox chemistry in the resulting sulfur dioxide-bound complexes.[9–13] Thus, for example, $MnI_2(OAsPh_3)_4$ reacts with sulfur dioxide to yield $Mn\{OS(O)I\}_2(OAsPPh_3)_3$, **I**, in which sulfur dioxide is inserted into a Mn–I bond. When complex **I** is heated in vaccum the novel compound Ph_3AsI_2, which has a four coordinate "spoke" structure $Ph_3AsI\text{-}I$, can be sublimed. On the other hand, exposing **I** to air results in the production of $[Ph_3AsI]I_3$ and $[(Ph_3AsO)_2H]I_3$, among other products.

We have previously reported[8b] that from the solid state reaction of $CoI_2(4\text{-CNpyO})_2(H_2O)_2$ (where 4-CNpyO is 4-cyanopyridine-*N*-oxide) with sulfur dioxide, we were able to obtain a complex of stoichiometry $CoI_2(4\text{-CNpyO})_2(SO_2)_{0.75}(H_2O)_2$, **II**. Allowing an ethanolic solution of **II** to interact with air led to the darkening of the solution and the formation of dark brown crystals, shown by single crystal X-ray analysis to be $[Co(4\text{-}EtO_2CpyO)_6](I_8)$ **III**. Although we are still investigating the chemistry involved in the production of **III**, here we wish to report its structure.

Apart from this, the hydrated manganese(II) iodide complex containing 4-methylpyridine-*N*-oxide as a ligand subsequently reacts with sulfur dioxide at room temperature to form $MnI_2(4\text{-}MepyO)_2(SO_2)_{0.75}(H_2O)_4$. When this previously reported complex[8e] is dissolved in ethanol and exposed to air for a month, reaction occurs to form a complex series of products, one of which, $[(4\text{-}MepyO)_2H](I_3)$, we have been able to separate and crystallographically characterise.

EXPERIMENTAL

We have prepared $CuCl_2(2,6\text{-}MepyO)_2(SO_2)_{0.5}(H_2O)_2$, $CuBr_2(3\text{-}HOH_2\text{-}CpyO)_2(SO_2)_{0.5}$, $MnI_2(4\text{-}MepyO)_2(SO_2)_{0.75}(H_2O)_4$ and $CoI_2(4\text{-}CNpyO)_2\text{-}(SO_2)_{0.75}(H_2O)_2$; their characterisation and coordination modes involving sulfur dioxide have been previously published.[8]

Ethanol or toluene solutions of these four SO_2 adducts were exposed to air at room temperature either by simply exposing them to air for about a month or by bubbling air into the solution for 4 h and subsequent stirring for 12 h. Using the former method, ethanolic solutions of $MnI_2\text{-}(4\text{-}MepyO)_2(SO_2)_{0.75}(H_2O)_4$ and $CoI_2(4\text{-}CNpyO)_2(SO_2)_{0.75}(H_2O)_2$ yield the crystalline decomposition products $[(4\text{-}MepyO)_2H](I_3)$ and $[Co(4\text{-}EtO_2\text{-}CpyO)_6](I_8)$ in low percentage. They were suitable for X-ray structure determination. Elemental analyses were performed by the University of Santiago de Compostela Microanalytical Services. *Anal.* Calcd. for $[(4\text{-}MepyO)_2\text{-}H](I_3)$ (%): C, 24.02; H, 2.52; N, 4.67. Found: C, 23.44; H, 2.78; N, 4.37. *Anal.* Calcd. for $[Co(4\text{-}EtO_2CpyO)_6](I_8)$ (%): C, 27.73; H, 2.60; N, 4.04. Found: C, 27.25; H, 2.41; N, 4.11. Furthermore, we have isolated and identified blue crystals of $CuSO_4 \cdot 5H_2O$ from a toluenic solution of $CuCl_2(2,6\text{-}MepyO)_2\text{-}(SO_2)_{0.5}(H_2O)_2$ and an ethanolic solution of $CuBr_2\text{-}(3\text{-}HO_2HCpyO)_2(SO_2)_{0.5}$ using the second method.

X-Ray Structure Determination of $[(4\text{-}MepyO)_2H](I_3)$

Crystallographic measurements were made at 230 K on a Rigaku AFC6S diffractometer operating with a $\omega\text{-}2\theta$ collection method and with graphite-monochromatised MoK_α radiation ($\lambda = 0.71069$ Å). Structure calculations were performed using the SHELXS package.[14] A linear correction factor was applied to the data. Hydrogen atoms were included in the structure factor calculations in idealised positions (C–H = 0.95 Å), and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. H11 sits on a centre of symmetry, fixing its coordinates. An empirical absorption correction was

TABLE I Experimental details and crystal data for [(4-MepyO)$_2$H](I_3^-)

Empirical formula	$C_{12}H_{15}N_2O_2I_3$
Formula weight	599.98
Temperature	23°C
Crystal system	Triclinic
Space group	$P\bar{1}$
Lattice Parameters:	$a = 12.703(3)$ Å $b = 14.127(4)$ Å $c = 7.939(2)$ Å $\alpha = 106.38(2)°$ $\beta = 92.69(3)°$ $\gamma = 86.56(3)°$
Volume	1364(1) Å^3
Z value	3
Diffractometer	Rigaku AFC6S
Scan type	$\omega/2\theta$
Radiation	MoK$_\alpha$ ($\lambda = 0.71069$ Å)
D_{calc}	2.191 g cm^{-3}
Linear absorption coefficient (MoK$_\alpha$)	51.03 cm^{-1}
$F(000)$	828
No. of reflections measured	Total: 1860 Unique: 1696 ($R_{int} = 0.237$)
Refinement	Full-matrix least-squares
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
No. observations ($I > 3.00\sigma(I)$)	678
No. variables	139
Goodness-of-fit indicator	3.09
Residuals: R; R_w	0.069; 0.070

made.[15] Maximum and minimum transmission coefficients were 1.08 and 0.88. The data were corrected for Lorentz and polarisation effects. No chemically significant peaks were observed in the final difference map (0.78 and $-1.10\,e^-\,Å^{-3}$). Crystal data for [(4-MepyO)$_2$H](I_3^-) are listed in Table I.

X-Ray Structure Determination of [Co(4-EtO$_2$CpyO)$_6$](I$_8$)

Crystallographic measurements were made at 293(2) K on an Enraf-Nonius CAD-4 diffractometer operating with a $\theta/2\theta$ collection method and with graphite-monochromatised MoK$_\alpha$ radiation ($\lambda = 0.71069$ Å). The crystal showed weak reflections, and beyond $2\theta > 40°$ the intensity values were less than 2σ, so they were not considered as being observed. The poor quality of crystals prevented the collection of improved data. Diffractometer data were processed by the PROFIT program[16] with profile analyses of reflections. Structure calculations were performed using the SHELXTL package.[17] An empirical absorption correction was made.[18] Maximum and minimum transmission coefficients were 0.844 and 0.526. Maximum peak

TABLE II Crystal and structure refinement data for $[Co(4\text{-}EtO_2\text{-}CpyO)_6](I_8^{2-})$

Empirical formula	$C_{16}H_{18}Co_{0.33}I_{2.67}N_2O_6$
Formula weight	692.37
Temperature	293(2) K
Crystal system	Trigonal
Space group	$R\bar{3}$
Lattice parameters:	$a = 17.021(2)$ Å $c = 19.063(4)$ Å
Volume	$4782.9(13)$ Å^3
Z value	9
Diffractometer	CAD-4
Scan type	$\theta/2\theta$
Radiation	MoK_α ($\lambda = 0.71069$ Å)
D_{calc}	$2.163\ mg\ m^{-3}$
Linear absorption coefficient	$4.211\ mm^{-1}$
$F(000)$	2937
Index ranges	$0 \leq h \leq 16,\ -16 \leq k \leq 0,\ 0 \leq l \leq 18$
Reflections collected	627
Independent reflections	563 $[R_{int} = 0.0321]$
Absorption correction	Empiric
Max. and min. transmission	0.844 and 0.526
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	560/0/133
Goodness-of-fit on F^2	1.099
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0345$, $wR2 = 0.0878$
Extinction coefficient	0.00000(7)

was $0.78\ e^-$ Å^{-3} and minimum peak was $-1.10\ e^-$ Å^{-3} in the final difference map. Crystal data for $[Co(4\text{-}EtO_2CpyO)_6](I_8^{2-})$ are shown in Table II.

Standard heavy-atom techniques were used to solve the structures followed by full-matrix least-squares (based on F^2 using the SHELXL-93 package[19] refinement. Hydrogen atoms were constrained to chemically reasonable positions with individual isotropic thermal parameters. All non-hydrogen atoms were treated anisotropically. Additional material comprising H-atom coordinates, thermal parameters, bond lengths and angles, and observed and calculated structure factors are available from the authors upon request.

RESULTS AND DISCUSSION

The diagnostic to distinguish the bonding mode for sulfur dioxide in adducts is typically based on infrared spectroscopy, but it should be noted that considerable overlap exists among the frequencies, especially between the $\nu(SO)$ η^1-S planar and ligand bound or η^1-S pyramidal and S-bridged.[2b] SO_2 lability studies are generally a good criterion to distinguish between some of these bonding modes, because SO_2 adducts with η^1-*S* pyramidal and ligand bound are labile and they lose sulfur dioxide easily, whereas desorption does not occur when sulfur dioxide is η^1-*S* planar or *S*-bridged. However, there is still doubt as to whether the labile sulfur dioxide is ligand bound or η^1-*S* pyramidal.

The tendency to form SO_4 adducts (normally studied by exposing of SO_2 adducts solutions to air) could be used as to help elucidate what coordination mode is present. Thus, the so-called Sulfato reaction, with rare exceptions, takes place with SO_2 adducts containing η^1-*S* pyramidal group[2b] but not by SO_2 adducts with ligand bound. In nearly all cases, when sulfate formation occurs, sulfate is coordinated in bidentate chelate fashion (η^2-SO_4) to the oxidised metal and is easily identifiable by $\nu(SO_4)$ frequencies[20] at 1296, 1172 and 880 and other bands near 856, 662, 610 and 549 cm^{-1}.

It is obvious that the redox process must involve sulfur dioxide, metal and atmospheric oxygen, and, as Kubas[2] said, other species different from coordinated sulfate may also be formed because of their decomposition. In this study, we have found that by exposing dilute ethanolic or toluenic (depending on solubility) solutions to air, the four SO_2 adducts studied experience a decomposition process. From these mixtures, a few crystals of $[(4\text{-MepyO})_2H](I_3)$ and $[Co(4\text{-EtO}_2CpyO)_6](I_8)$, were isolated. Concentration under vacuum of the filtrates gives solids for which elemental analyses indicate a complex mixture of products. Unfortunately, no other species could be identified. For $CuBr_2(3\text{-HOH}_2CpyO)_2(SO_2)_{0.5}$ and $CuCl_2(2,6\text{-MepyO})_2(SO_2)_{0.5}(H_2O)_2$ we found that they give, among other unidentified compounds, $CuSO_4 \cdot 5H_2O$, X-ray crystallographically characterised, as an oxidation product of SO_2. The same oxidation process had already been observed in the filtrates of a large number of reactions that we studied in toluene slurries and the isolation of $MnSO_4 \cdot H_2O$ and $CoSO_4 \cdot H_2O$ has been previously reported.[10b,11] On the other hand, it is well known that transition metals catalyse the oxidation of sulfur dioxide in the atmosphere. This oxidation has been observed in a large number of reactions studied in solution with Mn(II), Fe(III), Co(II), Cu(II) and Zn(II) complexes, where HSO_4^- and/or SO_4^{2-} were found, as aerobic degradation products of SO_2.[9–11]

We have found decomposition products derived from the ligand transformation promoted by the transition metal or from the transformation of SO_2 in sulfuric acid and its subsequent interaction with the neutral ligand. Thus, from the decomposition of an ethanolic solution of $MnI_2(4\text{-MepyO})_2(SO_2)_{0.75}(H_2O)_4$ a protonated ligand derivative, such as $[(4\text{-MepyO})_2H](I_3)$, shown in Figure 1, has been obtained. Although we are still investigating the chemistry involved in the production of these degradation species, the origin

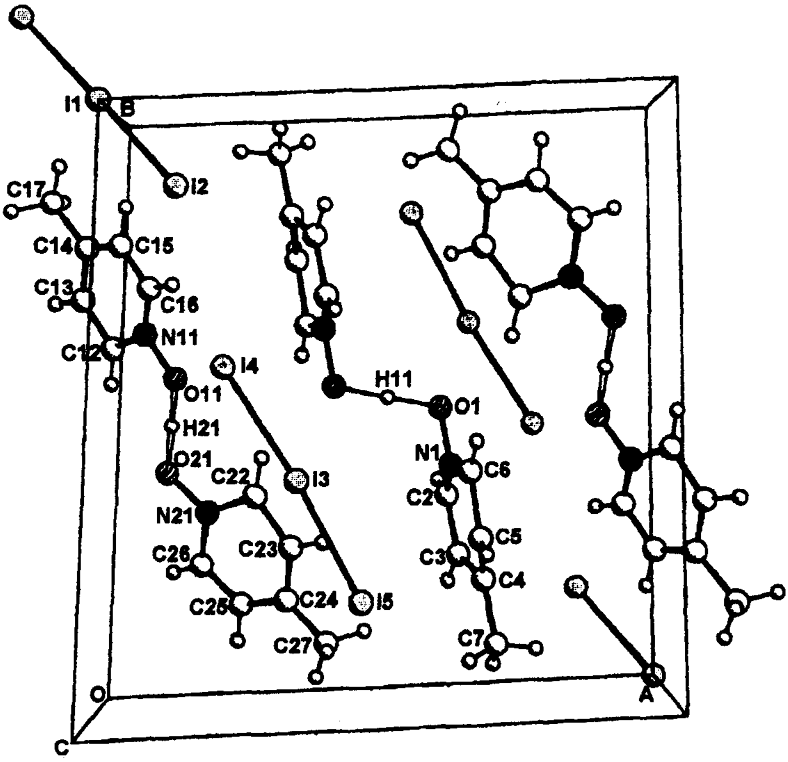

FIGURE 1 The structure of [(4-MepyO)$_2$H](I$_3$) showing the unit cell with the numbering scheme. Hydrogen atoms are given arbitrary thermal parameters for clarity.

of the bridging hydrogens H21 and H11 could possibly be the sulfuric acid obtained by oxidation of SO_2. Considering the pK_a values for H_2SO_4, the transfer of just one proton to 4-MepyO could be expected. Thus, Jonsson and Olovsson[21] have shown that one proton is transferred from H_2SO_4 to $MeCO_2H$ to give $MeC(O)OH_2$–HSO_4. This strongly suggests that the first proton of H_2SO_4 could be transferred to 4-MepyO. However, the transfer of a second proton is not so likely, since p$K_a(HSO_4^-)=1.92$ and it does not protonate 4-MepyO in the crystalline state. In fact, similar protonated ligand derivatives were described by us[10–12]. Thus, $(Ph_3PO)(Ph_3POH)$-(HSO_4) shows two triphenylphosphine oxide moieties, one of which is protonated, linked to the hydrogen sulfate anion by typical unsymmetrical hydrogen bonds [*e.g.*, O(1P)–H(1) = 1.06 Å and O(4S)–H(1) = 1.44 Å].

Moreover, iodine's propensity to catenate is well illustrated by numerous symmetrical and asymmetrical polyiodides which crystallise from solutions containing iodide ions and iodine. Stoichiometries of these crystals, and detailed geometry, markedly depend on the relative concentrations of the components as well as on the nature of the cation. In our case, triiodide arises from the degradation of $MnI_2(4\text{-}MepyO)_2(SO_2)_{0.75}(H_2O)_4$ and its subsequent oxidation.

In one of our other experiments, involving the decomposition of an ethanolic solution of $CoI_2(4\text{-}CNpyO)_2(SO_2)_{0.75}(H_2O)_2$, the new complex $[Co(4\text{-}EtO_2CpyO)_6](I_8)$ (Figure 2) was obtained, and its crystal structure determined by X-ray diffraction methods. The oxidation of neutral and anionic ligands as well as a change in the stoichiometry must be noted. Once again, the aerobic degradation of the cobalt SO_2 adduct in solution could produce sulfuric acid due to oxidation of SO_2. This acid could promote the cyanide group hydrolysis of the 4-CNpyO ligand to form a carboxylic acid group and, its subsequent reaction with ethanol could yield the corresponding ester group of the new ligand $4\text{-}EtO_2CpyO$.

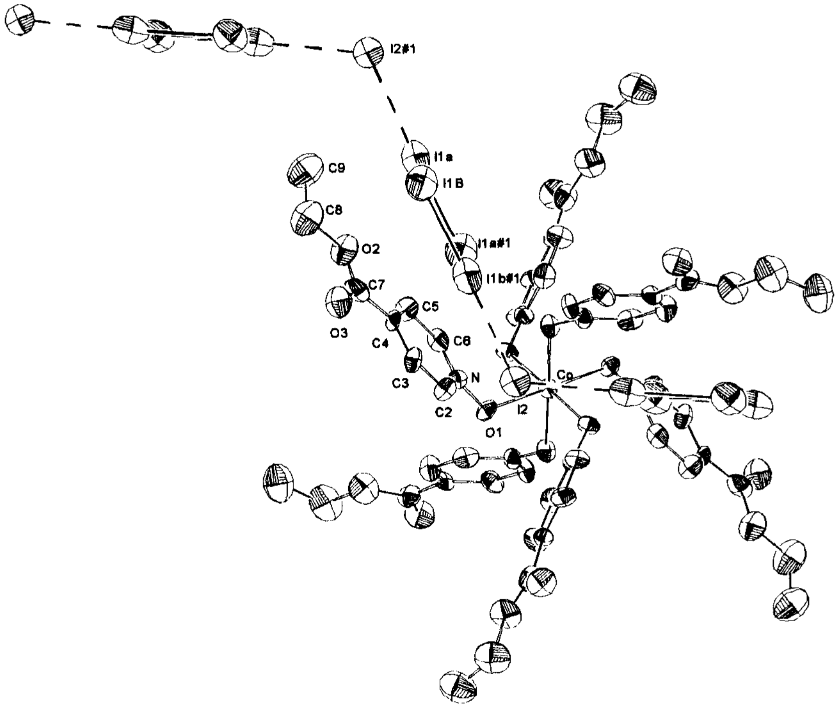

FIGURE 2 The structure of $[Co(4\text{-}EtO_2CpyO)_6](I_8)$ showing the labelling scheme (some atoms generated by symmetry operations also appear labelled). Hydrogen atoms are omitted for clarity. Two iodide anions interact with three iodine molecules, showing both disordered positions (only I1a–I1b#1 and I1b–Ia#1 with labels).

Finally, the reorganisation processes occurring during the transformation of $CoI_2(4\text{-}CNpyO)_2(SO_2)_{0.75}(H_2O)_4$ in $[Co(4\text{-}EtO_2CpyO)_6](I_8^{2-})$, such as changes in coordination number, oxidation, ligand changes, *etc.*, could also reflect similarities found in other case studies. For example, we could cite the case of a sulfur dioxide-saturated toluene slurry of the complex $CoI_2(Me_3PO)_2$, where cobalt is tetracoordinated,[11] and which yields $CoSO_4 \cdot H_2O$ (*via* SO_2 oxidation), $[Co(Me_3PO)_3(H_2O)_2]I_2$ and $[Co(Me_3PO)_3(H_2O)_3]I_2$, where cobalt is penta- and hexacoordinated, respectively, and where iodide changes from the first to the second coordination sphere.

It is seen then, that SO_2 can be oxidised to sulfuric acid and/or sulfate derivatives catalysed by Mn(II), Co(II) or Cu(II) species in solution, in the presence of air and moisture. Other very similar ligand derivatives as well as oxidation products of I^- or SO_2, obtained from reactions between SO_2 and metal precursors or from exposure to air of solutions of SO_2 adducts containing Ph_3PO, Ph_3AsO and Me_3PO, have been reported by us[9–13] and are listed in Table III. $MnI_2(4\text{-}MepyO)_2(SO_2)_{0.75}(H_2O)_4$ to air resulted in the formation of brown crystals of $[(4\text{-}MepyO)_2H](I_3)$.

The molecular structure of $[(4\text{-}MepyO)_2H](I_3)$ is shown in Figure 1. Positional parameters and selected bond lengths and angles are given in Tables IV and V, respectively. It is remarkable that both 4-MepyO moieties are linked by a short symmetrical hydrogen bond, as O11–H21 (1.245 Å) and H21–O21 (1.237 Å) distances show. It must be noted that bridging protons were restricted to idealised positions in the structure determination. These distances are considerably shorter than the sum of van der Waals' radii ($O\text{–}H \approx 2.7$ Å, using the values $O = 1.5$ Å and $H \approx 1.2$ Å). We also point out that the global O11–O21 distance is only 2.5(1) Å, whereas double the oxygen van der Waals' radius is 3.0 Å. A similar distance was found[12] for $[(Ph_3AsO)_2H]I_3$. Another example of a cation showing a strong symmetrical hydrogen bond is *bis*(*N*-nitrosopyrrolidine) hydrogen hexafluorophosphate,[22] where the $O \cdots O$ distance is 2.47 Å.

In the triiodide anion, the distances I3–I4 (2.89 Å) and I3–I5 (2.94 Å) are considerably shorter than the sum of van der Waals' radii (4.3 Å), and the I4–I3–I5 angle (175.3°) agrees with the expected values for a nearly symmetrical linear triatomic polyiodide anion.[12,23]

In other experiments, we studied the oxidation of an ethanolic solution of $CoI_2(4\text{-}CNpyO)_2(SO_2)_{0.75}(H_2O)_2$, obtained by the interaction of $CoI_2(4\text{-}CNpyO)_2(H_2O)_2$ with SO_2 in the solid state, and which resulted in the formation of a dark brown crystalline solid. This has been identified as $[Co(4\text{-}EtO_2CpyO)_6](I_8)$ by single-crystal X-ray studies. These crystals diffracted poorly and data collected are not of very high quality;

TABLE III Some well-characterised products isolated in the aerobic oxidation of SO_2 adducts or in the reaction between SO_2 and metal precursors in air

SO_2 adduct	*Solvent*	*Decomposition products*	*Reference*
Neutral ligand with N–O bond			
$CuCl_2(2,6\text{-}MepyO)_2(SO_2)_{0.5}(H_2O)_2$	Toluene	$CuSO_4 \cdot 5H_2O$	This work
$CuBr_2(3\text{-}HOH_2CpyO)_2(SO_2)_{0.5}$	Ethanol	$CuSO_4 \cdot 5H_2O$	This work
$MnI_2(4\text{-}MepyO)_2(SO_2)_{0.75}(H_2O)_4$	Ethanol	$[(4\text{-}MepyO)_2H](I_3^-)$	This work
$CoI_2(4\text{-}CNpyO)_2(SO_2)_{0.75}(H_2O)_2$	Ethanol	$[Co(4\text{-}EtO_2CpyO)_6](I_8^{2-})$	This work
Neutral ligand with P–O bond			
$[FeCl_2(Ph_3PO)_4][FeCl_4] + SO_2$	Toluene	$(Ph_3PO)(Ph_3POH)(HSO_4)$	9
$[Fe\{OS(O)Br\}_2(Ph_3PO)_4][FeBr_4]$	Toluene	$(Ph_3PO)(Ph_3POH)(HSO_4)$	9
$CoI_2(Ph_3PO)_2 + SO_2$	Toluene	$I_2 + (Ph_3PO)(Ph_3POH)(HSO_4) + CoSO_4 \cdot H_2O$	11
$CoI_2(Me_3PO)_2 + SO_2$	Toluene	$[Co(Me_3PO)_3(H_2O)_2]I_2 + [Co(Me_3PO)_3(H_2O)_3]I_2 + CoSO_4 \cdot H_2O$	11
$ZnI_2(Ph_3PO)_2(SO_2)_{0.5}(H_2O)_3$	Toluene	$(Ph_3PO)(Ph_3POH)(HSO_4)$	Unpublished work
$Mn(NCS)_2(Ph_3PO)_4(SO_2)$	Toluene	$(Ph_3PO)(Ph_3POH)(HSO_4)$	10a
$Mn\{OPPh_2(OPh)\}_4I_2 + SO_2$	Toluene	$MnSO_4 \cdot H_2O + OPPh_2(OPh) + I_2$	10b
$Co(NCS)_2(Ph_3PO)_2 + SO_2$	Toluene	$(Ph_3PO)(Ph_3POH)(HSO_4) + CoSO_4 \cdot H_2O$	11
Neutral ligand with As–O bond			
$[Fe\{OS(O)Cl\}_2(Ph_3AsO)_4][FeCl_4]$	Toluene	$(Ph_3AsOH)(HSO_4)$	9
$[Fe\{OS(O)Br\}_2(Ph_3AsO)_4][FeBr_4]$	Toluene	$(Ph_3AsOH)(HSO_4)$	9
$Mn\{OS(O)I\}_2(Ph_3AsO)_3$	Toluene	Ph_3AsI_2,	13
$Mn\{OS(O)I\}_2(Ph_3AsO)_3$	Toluene	$[Ph_3AsI]I_3$, $[(Ph_3AsO)_2H]I_3$	12
$CoI_2(Ph_3AsO)_2 + SO_2$	Toluene	$I_2 + (Ph_3AsOH)(HSO_4) + CoSO_4 \cdot H_2O + [Ph_3AsI]I_3$	11
$Co(NCS)_2(Ph_3AsO)_2 + SO_2$	Toluene	$(Ph_3AsOH)(HSO_4) + CoSO_4 \cdot H_2O$	11

TABLE IV Positional parameters and $B(eq)$ values (Å^2) for $[(4\text{-MepyO})_2\text{H}](\text{I}_3)$

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
I1	0	1	1	4.4(5)
I2	0.1390(5)	0.8499(5)	1.0862(9)	6.7(4)
I3	0.3486(5)	0.3763(5)	0.9036(8)	4.8(4)
I4	0.2239(5)	0.5603(5)	0.9689(9)	6.5(4)
I5	0.4607(5)	0.1814(5)	0.8192(8)	6.3(4)
O1	0.595(4)	0.479(6)	0.467(8)	9(2)
N1	0.615(4)	0.382(6)	0.43(1)	4(2)
H11	0.5	0.5	0.5	4.0
C2	0.610(5)	0.329(7)	0.27(1)	3(2)
C3	0.632(5)	0.229(6)	0.26(1)	3(2)
C4	0.676(6)	0.191(7)	0.39(1)	4(2)
C5	0.668(5)	0.263(7)	0.55(1)	4(2)
C6	0.648(7)	0.373(8)	0.58(1)	8(2)
C7	0.700(6)	0.085(8)	0.38(1)	7(2)
O11	0.123(6)	0.544(6)	0.47(1)	12(2)
N11	0.065(6)	0.620(7)	0.46(1)	6(2)
C12	0.001(6)	0.599(6)	0.32(1)	3(2)
C13	−0.056(6)	0.685(8)	0.32(1)	5(2)
C14	−0.046(7)	0.771(7)	0.43(1)	4(2)
C15	0.020(7)	0.770(7)	0.55(1)	5(2)
C16	0.075(6)	0.696(6)	0.57(1)	4(2)
C17	−0.114(7)	0.853(7)	0.39(1)	8(2)
O21	0.103(5)	0.382(5)	0.249(8)	9(2)
N21	0.179(5)	0.313(6)	0.258(9)	5(2)
H21	0.1146	0.4638	0.3578	4.0
C22	0.266(5)	0.341(5)	0.379(8)	1(2)
C23	0.332(6)	0.254(8)	0.37(1)	5(2)
C24	0.324(6)	0.165(7)	0.27(1)	3(2)
C25	0.241(7)	0.155(7)	0.16(1)	5(2)
C26	0.167(6)	0.222(7)	0.14(1)	4(2)
C27	0.397(8)	0.092(8)	0.28(1)	8(2)

nevertheless, resolution of the crystal structure was supposed to be the best way of characterisation of this oxidation product. The conformations of cation and anion surroundings, with the corresponding atomic numbering scheme, are shown in Figure 2. Atomic coordinates are listed in Table VI and selected bond lengths and angles are given in Table VII. The coordination environment around the cobalt(II) centre consists of a slightly distorted octahedron surrounded by six oxygens belonging to 4-carboethoxypyridine-*N*-oxide ligands.

A comparative study of $[\text{Co}(4\text{-EtO}_2\text{CpyO})_6](\text{I}_8)$ with its analogues of pyridine-*N*-oxide[24] and 4-methylpyridine-*N*-oxide[25] with different counterions, such as nitrate or perchlorate, shows that slight distortion from perfect octahedral symmetry, is more similar to that shown by the pyO derivative, than to the tetragonal distortion caused by Jahn–Teller forces[24] present in the 4-MepyO derivative. In the case at hand, the metal–ligand bond length is

TABLE V Selected bond lengths (Å) and angles (°) for $[(4\text{-MepyO})_2H](I_5^-)$

Atom	*Atom*	*Lengths*	*Atom*	*Atom*	*Atom*	*Angles*
I1	I2	2.887(7)	I4	I3	I5	175.3(3)
I3	I4	2.89(1)	N1	O1	H11	110.75
I3	I5	2.94(1)	O1	N1	C2	120(8)
O1	H11	1.246	O1	N1	C6	100(8)
O1	N1	1.33(8)	C2	N1	C6	139(10)
N1	C2	1.28(7)	N1	C2	C3	109(8)
N1	C6	1.31(9)	C2	C3	C4	129(8)
C2	C3	1.41(9)	C3	C4	C5	107(9)
C3	C4	1.37(9)	C3	C4	C7	127(8)
C4	C5	1.35(9)	C5	C4	C7	123(9)
C4	C7	1.5(1)	C4	C5	C6	130(9)
C5	C6	1.5(1)	N1	C6	C5	103(8)
O11	H21	1.245	N11	O11	H21	118.16
O11	O21	2.5(1)	O11	N11	C12	114(10)
O11	N11	1.30(9)	O11	N11	C16	117(10)
N11	H21	2.183	C12	N11	C16	130(10)
N11	C12	1.32(8)	N11	C12	C13	106(8)
N11	C16	1.20(9)	C12	C13	C14	130(9)
C12	C13	1.4(1)	C13	C14	C15	112(10)
C13	C14	1.3(1)	C13	C14	C17	117(10)
C14	C15	1.23(9)	C15	C14	C17	131(11)
C14	C17	1.5(1)	C14	C15	C16	127(10)
C15	C16	1.3(1)	N11	C16	C15	116(9)
O21	H21	1.237	N21	O21	H21	114.66
O21	N21	1.35(8)	O21	N21	C22	118(8)
N21	H21	2.176	O21	N21	C26	115(7)
N21	C22	1.42(7)	C22	N21	C26	127(7)
N21	C26	1.39(8)	N21	C22	C23	108(7)
C22	C23	1.4(1)	C22	C23	C24	129(9)
C23	C24	1.29(9)	C23	C24	C25	114(10)
C24	C25	1.36(9)	C23	C24	C27	121(9)
C24	C27	1.4(1)	C25	C24	C27	125(10)
C25	C26	1.3(1)	C24	C25	C26	129(9)
			N21	C26	C25	112(7)

TABLE VI Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^{-3}$) for $[Co(4\text{-EtO}_2\text{CpyO})_6](I_8^{2-})$

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
I2	0	0	3360(1)	69(1)
I1a*	2264(3)	4525(3)	3292(2)	71(1)
I1b*	1971(3)	4050(3)	3407(3)	84(2)
Co	0	0	0	23(1)
O1	−953(5)	52(5)	648(4)	31(2)
N	−780(6)	748(7)	1052(5)	29(2)
C2	−1005(8)	604(8)	1747(5)	30(3)
C3	−882(8)	1299(9)	2155(6)	38(3)
C4	−523(7)	2146(8)	1911(6)	30(3)
C5	−270(8)	2306(8)	1204(6)	40(3)
C6	−411(8)	1578(9)	803(6)	35(3)
C7	−442(9)	2881(10)	2386(8)	47(4)
C8	120(12)	4473(11)	2499(7)	77(5)
C9	781(12)	5317(12)	2147(8)	86(5)
O2	11(6)	3695(7)	2096(5)	61(3)
O3	−770(6)	2768(6)	2956(5)	62(2)

*Site occupancy factor 0.5.

TABLE VII Selected bond lengths (Å) and angles (°) for $[Co(4\text{-}EtO_2CpyO)_6](I_8^{2-})$

Atoms	*Lengths*	*Atoms*	*Angles*
I2–I1a#1	3.157(6)	I1a#1–I2–I1a#2	119.995(3)
I2–I1b#1	3.863(6)	I1a#1–I2–I1a#3	119.991(3)
I1a–I1b#1	2.815(6)	I1a#2–I2–I1a#3	119.991(3)
I2–I1a#3	3.157(6)	I1b#1–I1a–I2#1	178.07(10)
I1a–I1b	0.739(4)	I1b–I1a–I2#1	160.6(8)
I1b–I1b#1	2.140(8)	I1b–I1a–I1b#1	20.8(8)
Co–O1	2.076(7)	I1a–I1b–I1b#1	152.2(10)
Co–O1#4	2.076(7)	I1a–I1b–I1a#1	159.2(8)
Co–O1#5	2.076(7)	I1b#1–I1b–I1a#1	7.0(2)
Co–O1#6	2.076(7)	I1b-I1a#3-I(2)	178.1(3)
Co–O1#4	2.076(7)	O1–Co–O1#4	88.2(3)
Co–O1#7	2.076(7)	O1–Co–O1#5	88.2(3)
O1–N	1.317(10)	O1–Co–O1#6	91.8(3)
N–C6	1.315(13)	O1–Co–O1#4	91.8(3)
N–C2	1.366(13)	O1–Co–O1#7	180
C2–C3	1.34(2)	N–O1–Co	124.0(6)
C3–C4	1.34(2)	C6–N–O1	121.8(9)
C4–C5	1.40(2)	O1–N–C2	119.2(9)
C4–C7	1.49(2)	C6–N–C2	119.0(10)
C5–C6	1.37(2)	C3–C2–N	119.8(10)
C8–C9	1.47(2)	N–C6–C5	122.9(10)
O2–C7	1.32(2)	C4–C3–C2	122.4(10)
O2–C8	1.46(2)	C3–C4–C5	118.3(10)
O3–C7	1.194(14)	C6–C5–C4	117.6(10)
		C3–C4–C7	119.6(11)
		C5–C4–C7	122.0(12)
		C7–O2–C8	118.3(11)
		O3–C7–O2	122.0(14)
		O3–C7–C4	125.2(12)
		O2–C7–C4	112.7(12)
		O2–C8–C9	109.5(12)

Symmetry transformations used to generate equivalent atoms: #1: $-x+\frac{1}{3}, -y+\frac{2}{3}, -z+\frac{2}{3}$; #2: $y-\frac{2}{3}, -x+y-\frac{1}{3}, -z+\frac{2}{3}$; #3: $x-y+\frac{1}{3}, x-\frac{1}{3}, -z+\frac{2}{3}$; #4: $x-y, x, -z$; #5: $-x+y, -x, z$; #6: $y, -x+y, -z$; #7: $-x, -y, -z$.

2.076 Å, slightly shorter than 2.090 Å observed for $[Co(pyO)_6](NO_3)_2$.[24] A slightly shorter N–O bond length is also observed for our ligand.

The molecular structure is distinguished by the dinegative polyiodide I_8^{2-}, of which some similar features are found in literature.[26] Polyiodide anions could be considered as Lewis acid–base complexes where I^- or I_3^- act as bases and I_2 as acid. The bond lengths (longer than that found for solid I_2, *ca* 2.68 Å) suggest that it can be regarded as a chain of associated I^- or I_3^- and I_2 units. Thus, alternatively, it could be described as two iodide anions interacting with three iodine molecules which features a planar Z-shaped array, *i.e.*, $[(I_2)I^-(I_2)I^-(I_2)]$. This is shown in Figure 2 together with the atom labelling and the disorder found for the iodine molecule. The 50% occupancy of each iodine (I1a and I1b) is compatible with a disorder model in which the presence of I1a in a given site is accompanied by the presence of an I1b ion, at a distance of 2.815(6) Å.

The trigonal symmetry of the crystal structure determines the angles of 120° formed by iodine molecules surrounding iodide ions (I2). Values of the distances I1a–I1b#1 (2.815 Å) and I2–I1a#3 (3.157 Å) are considerably shorter than the sum of van der Waals' radii (4.3 Å). These lengths and the angle I1b–I1a#3–I2 (178.1°) are close to expected values for asymmetrical polyiodide anions[23] (*e.g.*, 2.82 Å, 3.10 Å and 177°, respectively).

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