DALTON
FULL PAPER

Cobalt(II) aldoxime complexes stabilised by halide hydrogen bonding: crystal structures of [Co{HON=C(H)(Me)}$_4$X$_2$] (X = Cl or Br) and [Co{HON=C(H)(Pr)}$_4$Cl$_2$]

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Starting from the metal halide hydrates and the simple monoximes butyraldoxime (bax) and acetaldoxime (aax), under dehydrating conditions by the use of trimethyl orthoformate, complexes of general formula [Co(L)$_4$X$_2$] (L = aax or bax; X = Cl or Br) and [Mn(bax)$_4$Cl$_2$] have been obtained. Complexes [Co(bax)$_4$Cl$_2$], [Co(aax)$_4$Cl$_2$] and [Co(aax)$_4$Br$_2$] have been structurally characterised using single crystal X-ray diffraction. All three contain mononuclear octahedral cobalt ions which are stabilised by intramolecular hydrogen-bonding interactions. Strong intermolecular hydrogen-bonding interactions are present only in [Co(aax)$_4$Cl$_2$]. Spectroscopic studies indicate that the manganese aax and bax complexes obtained are similar to the cobalt analogues. The manganese compounds, however, are much less stable thereby thwarting the isolation of crystals for structure determination. The isolated coordination complexes are all highly reactive towards atmospheric water and readily decompose to yield the metal hydrates.

Several articles describe the synthetic and structural chemistry of transition metal oxime complexes with palladium, platinum or nickel.[1] However, properly described cobalt and manganese compounds of simple mono-oximes are extremely scarce,[2] in contrast to the most extensively studied model compounds for the vitamin B-12 cofactor which are cobalt complexes of the *vic*-dioxime dimethylglyoxime (H$_2$dmg).[3] Our current interest in autoxidation drying mechanisms[4] occurring in alkyd paints, in which both cobalt catalysts and simple oximes are present as additives,[5] led us to investigate cobalt ketoxime and aldoxime coordination chemistry. Indeed, species formed from oxime additives in the presence of cobalt have received unexpectedly little attention, despite their possible crucial role in the stability and the drying properties of the paints.[5,6]

The current investigations started with a study of the complexation properties of butanone oxime with cobalt salts. From hydrated cobalt chloride, very air-sensitive cobalt/butanone oxime species were obtained.[6] Recrystallisation resulted in the unique polymeric structure [{Co$_4$(μ-Cl)$_6$Cl$_2$(thf)$_4$(H$_2$O)$_2$}·2THF]$_n$, but unfortunately the compound did not contain butanone oxime as a ligand.[7] The first acetal diimine cobalt(II) complex [CoI$_2${((Et)(Me)C=NO)$_2$C(Me)$_2$}] was isolated from cobalt iodide in acetone. The chelating acetal diimine ligand was formed *in situ* by metal-mediated condensation of two butanone oxime molecules with acetone in the presence of trimethyl orthoformate.[8] These examples clearly show the difficulties in stabilising and isolating monodentate cobalt(II) ketoxime complexes compared to the palladium and platinum ketoxime derivatives which have been thoroughly studied.[9] This manuscript describes an extension of these investigations of the coordination of aldoximes to cobalt and manganese halide salts, to gain further insight into their possible interactions in paints. Although previous reports describe cobalt, nickel or copper aldoxime complexes,[2] few give accurate synthetic procedures or explicit spectroscopic or structural data.[10]

Experimental

Materials and instrumentation

Butyraldoxime (bax) and acetaldoxime (aax) were provided by Condea Servo (Delden, The Netherlands). All other chemicals and solvents were commercially available and used without further purification. The metal content of the complexes was determined by complexometric titration with Na$_2$H$_2$edta. The chloride contents were determined using a potentiometric titration with silver nitrate (Volhard method). The C, H and N contents were measured on a Perkin-Elmer 2400 Series II analyser. The infrared spectra (4000–300 cm^{-1}) were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. Solid-state ligand field spectra (Vis-NIR) were obtained on a Perkin-Elmer Lambda 900 spectrophotometer, using the diffuse reflectance technique, with MgO as a reference.

Synthesis of the complexes

In a typical procedure 5.4 mmol of the metal salt were covered by an excess of trimethyl orthoformate and then dissolved in 10 ml of solvent. A solution of 21.6 mmol of the aldoxime ligand was prepared in 10 ml of the same solvent. Both solutions were warmed and mixed. The mixture was boiled until the final volume was reduced to approximately 10 ml. The resulting solution was allowed to stand under ambient atmosphere for 2 to 24 hours, to yield crystals after slow evaporation of the remaining solvent. In all the syntheses 1.5 equivalents of trimethyl orthoformate were used (per molecule of water present in the metal hydrates) as dehydrating agent.

[Co(bax)$_4$Cl$_2$] 1. Syntheses can be carried out in methanol, ethanol, isopropyl alcohol or chloroform. Starting from CoCl$_2$·6H$_2$O a red-pink crystalline material was recovered in

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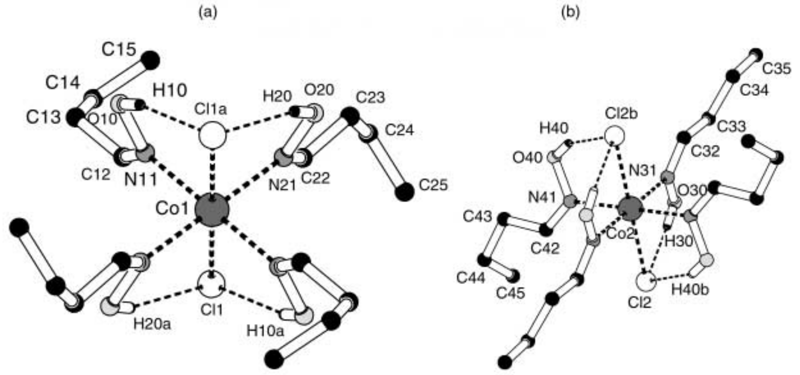

Fig. 1 A PLUTON projection of the two independent molecules of [Co(bax)$_4$Cl$_2$] **1** with atom labels. Only the hydrogen atoms involved in hydrogen bonding are shown.

95% yield from each of these solvents. Calc. for C$_{16}$H$_{36}$Cl$_2$CoN$_4$O$_4$: C, 40.5; H, 6.8; Cl, 15.0; Co, 12.4; N, 11.8%. Found: C, 37.1; H, 6.7; Cl, 13.8; Co, 13.1; N, 11.0%. mp = 66–68 °C. Selected IR bands, cm^{-1}: 3260s, br, OH stretching; 2961m, 2933w, 2873w, CH stretching; 1669w, C=N stretching; 1427vs, 1380m, 1342m, CH bending; 1128w, 986w, 934vs, 704m, 592vs, br. Vis-NIR (solid state) (10^3 cm^{-1}): 30.0, 19.6, 8.7 and 6.3.

[Co(bax)$_4$Br$_2$] 2. Syntheses were carried out in methanol, ethanol, Pr^{i}OH or chloroform. Starting from CoBr$_2$·6H$_2$O dark purple crystals were recovered in 95% yield. Calc. for C$_{16}$H$_{36}$Br$_2$CoN$_4$O$_4$: C, 33.8; H, 6.4; N, 9.9%. Found: C, 31.1; H, 6.3; N, 9.7%. mp = 66–68 °C. Selected IR bands, cm^{-1}: 3272s, br, OH stretching; 2959m, 2935w, 2873w, CH stretching; 1665w, C=N stretching; 1419vs, 1382w, 1338m, CH bending; 1128w, 983w, 930vs, 703m, 566s, br. Vis-NIR (solid state) (10^3 cm^{-1}): 38.6, 33.3, 19.5, 15.4, 8.7 and 6.3.

[Mn(bax)$_4$Cl$_2$] 3. Synthesis was carried out in methanol. Starting from MnCl$_2$·4H$_2$O very air-sensitive, thin white needles were recovered in less than 10% yield; the starting salt recrystallised in majority. Rapid decomposition of the compound did not allow satisfactory elemental analyses. mp = 100 °C (decomp.). Selected IR bands, cm^{-1}: 3300s, br, OH stretching; 2964m, 2935w, 2876w, CH stretching; 1670w, C=N stretching; 1428vs, 1382w, 1344m, CH bending; 1126w, 981w, 930vs, 701m, 591vs, br.

[Co(aax)$_4$Cl$_2$] 4. Syntheses were carried out in methanol or ethanol starting from CoCl$_2$·6H$_2$O. Violet prisms were obtained in 45% yield. Possibly the high solubility of the compound precludes higher yields. Calc. for C$_8$H$_{20}$Cl$_2$CoN$_4$O$_4$: C, 26.2; H, 5.5; Cl, 19.4; Co, 16.1; N, 15.3%. Found: C, 25.5; H, 5.2; Cl, 18.8; Co, 17.1; N, 15.6%. mp = 170 °C (decomp.). Selected IR bands, cm^{-1}: 3262s, br, OH stretching; 1671w, C=N stretching; 1404m, CH bending, 1318m, 1121m, 1018w, 932s, 841m, 694vs, 641m, 553s, 483m. Vis-NIR (solid state) (10^3 cm^{-1}): 38.8, 33.3, 19.1, 15.0, 8.8 and 6.3.

[Co(aax)$_4$Br$_2$] 5. Synthesis was carried out in methanol starting from CoBr$_2$·6H$_2$O. Long purple needles were obtained in 92% yield. Calc. for C$_8$H$_{20}$Br$_2$CoN$_4$O$_4$: C, 21.1; H, 4.4; N, 12.3%. Found: C, 20.7; H, 4.4; N, 12.3%. mp = 130–132 °C. Selected IR bands, cm^{-1}: 3244s, br, OH stretching; 1668w, C=N stretching; 1409m, CH bending; 1317m, 1115m, br, 934vs, 837s, 698vs, 594m, 542s, br, 481m. Vis-NIR (solid state) (10^3 cm^{-1}): 31.2, 21.2, 17.9, 15.4, 14.1, 8.8 and 6.3.

Structure determinations of [Co{HON=C(H)(Pr)}$_4$Cl$_2$] 1, [Co{HON=C(H)(Me)}$_4$Cl$_2$] 4 and [Co{HON=C(H)(Me)}$_4$Br$_2$] 5

The crystal data and refinement parameters for complexes **1**, **4** and **5** are collected in Table 1. For [Co{HON=C(H)(Pr)}$_4$Cl$_2$] the high solubility both in polar and apolar solvents made recrystallisation difficult. Suitable single crystals for X-ray diffraction were obtained from a highly concentrated solution in hexane kept at −20 °C for 24 hours. Suitable crystals of [Co{HON=C(H)(Me)}$_4$Cl$_2$] were grown directly from reaction mixtures. Samples of [Co{HON=C(H)(Me)}$_4$Br$_2$] were recovered from a toluene–hexane two-layer recrystallisation. Data were collected on a Nonius Kappa CCD area detector with rotating anode, λ(Mo-Kα) = 0.71073 Å, using a graphite monochromator. Absorption corrections based on multiple measured equivalent reflections were applied to each compound.

The structures were solved by Patterson techniques (DIRDIF 99[11]) and refined using full matrix least squares on F^2 (SHELXL 97[12]). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms, except those on hydroxyl oxygens, were located at calculated positions and refined riding on their carrier atoms. The hydroxyl hydrogens [H(10), H(20), H(30) and H(40) in complex **1**, H(1) and H(2) in both **4** and **5**] were located in the Fourier difference synthesis, and their positional and displacement parameters freely refined. Geometric calculations and molecular graphics were performed with PLATON.[13]

CCDC reference number 186/2270.

See http://www.rsc.org/suppdata/dt/b0/b007919g/ for crystallographic files in .cif format.

Results and discussion

Description of the structures

[Co(bax)$_4$Cl$_2$] 1. A projection of the structure of complex **1** is given in Fig. 1. Relevant bond lengths and angles are collected in Table 2. The unit cell contains two independent molecules in which the cobalt ions reside on crystallographic inversion centres. The cobalt ions in both molecules are in an octahedral configuration with four nitrogen donors of the butyraldoxime molecules in the equatorial plane and two chlorides in the axial positions. Intramolecular hydrogen-bonding interactions from the oxime O–H to the chloride atoms are present. The two independent molecules differ in the configuration of the oxime ligands, as shown in the projection of **1** (Fig. 1). An attempt is made to show these differences and therefore the representations of the two molecules do not reflect the relative positions in the crystal lattice. The two independent molecules are structurally different due to the distinct ligand conformations, *gauche* (synclinal) or *anti* (anti-periplanar), around the C–C bonds of the butyl group. The conformations of the butyl groups in molecule 1 are *gauche*/*gauche* (N11 · · · C15) and *anti*/*gauche* (N21 · · · C25), whereas in molecule 2 they are *anti*/*anti* (N31 · · · C35) and *anti*/*gauche* (N41 · · · C45). Intermolecular interactions, other than the normal van der Waals interactions, are not observed between the two molecules.

Table 1 Crystal and refinement data for [Co(bax)$_4$Cl$_2$] **1**, [Co(aax)$_4$Cl$_2$] **4** and [Co(aax)$_4$Br$_2$] **5**

	1	**4**	**5**
Formula	$C_{16}H_{36}Cl_2CoN_4O_4$	$C_8H_{20}Cl_2CoN_4O_4$	$C_8H_{20}Br_2CoN_4O_4$
M_r	478.32	366.11	455.03
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
Crystal system	Triclinic	Triclinic	Monoclinic
a/Å	7.4864(1)	7.4892(2)	7.5824(2)
b/Å	12.7386(3)	7.7050(3)	12.1368(4)
c/Å	12.7471(3)	8.6242(3)	9.2141(3)
α/°	84.1284(10)	100.6597(14)	
β/°	87.0347(12)	115.3716(19)	94.7954(17)
γ/°	88.4322(10)	107.584(2)	
V/Å^3	1207.35(4)	399.06(2)	844.97(5)
μ(Mo-Kα)/mm^{-1}	0.958	1.423	5.757
T/K	150	150	150
Z	2	1	2
Reflections collected	19232	4206	6544
No. unique reflections	5798	1780	1930
R_{int}	0.058	0.042	0.082
$R1$ [$I > 2\sigma(I)$]	0.0294	0.0279	0.0287
$wR2$ [all data]	0.0727	0.0684	0.0701

Table 2 Selected geometric parameters for the two independent molecules of complex **1**: bond lengths (Å), bond and torsion angles (°), and hydrogen-bonding geometries (Å and °)

Molecule 1		Molecule 2	
Co(1)–Cl(1)	2.4665(3)	Co(2)–Cl(2)	2.4515(3)
Co(1)–N(11)	2.1611(12)	Co(2)–N(31)	2.1510(12)
Co(1)–N(21)	2.1585(12)	Co(2)–N(41)	2.1583(12)
Cl(1)–Co(1)–N(11)	91.96(3)	Cl(2)–Co(2)–N(31)	88.81(3)
Cl(1)–Co(1)–N(21)	91.63(3)	Cl(2)–Co(2)–N(41)	91.24(3)
N(11)–Co(1)–N(21)	89.05(4)	N(31)–Co(2)–N(41)	88.63(4)
N(11)–C(12)–C(13)–C(14)	−134.17(18)	N(31)–C(32)–C(33)–C(34)	−166.02(18)
C(12)–C(13)–C(14)–C(15)	63.4(2)	C(32)–C(33)–C(34)–C(35)	−176.68(17)
N(21)–C(22)–C(23)–C(24)	−173.11(15)	N(41)–C(42)–C(43)–C(44)	175.36(15)
C(22)–C(23)–C(24)–C(25)	70.2(2)	C(42)–C(43)–C(44)–C(45)	−69.09(19)
H(10) $\cdots$ Cl(1)^a	2.30(2)	H(30) $\cdots$ Cl(2)	2.32(2)
O(10) $\cdots$ Cl(1)^a	3.038(1)	O(30) $\cdots$ Cl(2)	3.047(1)
H(20) $\cdots$ Cl(1)^a	2.26(2)	H(40) $\cdots$ Cl(2)^b	2.32(2)
O(20) $\cdots$ Cl(1)^a	3.006(1)	O(40) $\cdots$ Cl(2)^b	3.055(1)
O(10)–H(10) $\cdots$ Cl(1)^a	154(2)	O(30)–H(30) $\cdots$ Cl(2)	155(2)
O(20)–H(20) $\cdots$ Cl(1)^a	159(2)	O(40)–H(40) $\cdots$ Cl(2)^b	154(2)

Symmetry operations: ^{a} $1 - x, 1 - y, 1 - z$; ^{b} $2 - x, -y, -z$.

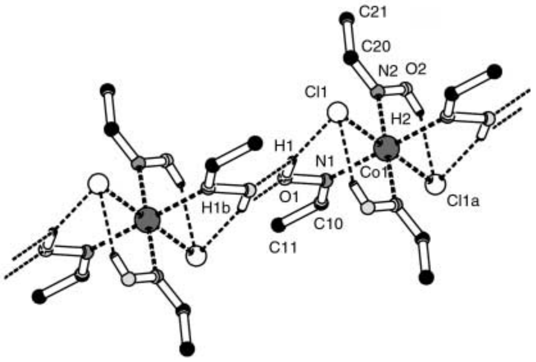

Fig. 2 A PLUTON projection of [Co(aax)$_4$Cl$_2$] **4**. Details as in Fig. 1.

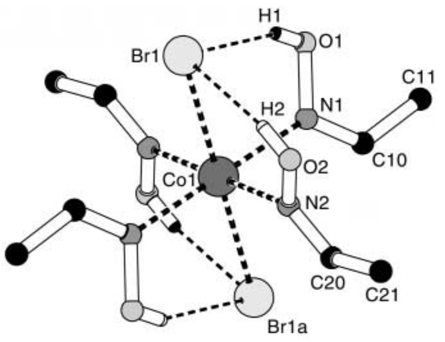

Fig. 3 A PLUTON projection of [Co(aax)$_4$Br$_2$] **5**. Details as in Fig. 1.

[Co(aax)$_4$Cl$_2$] 4 and [Co(aax)$_4$Br$_2$] 5. Projections of the crystal structures of complexes **4** and **5** are shown in Figs. 2 and 3, respectively, whilst selected parameters are given in Table 3. The unit cell of **4** (space group $P\bar{1}$) contains one molecule. The cobalt ion is in an octahedral geometry formed by the nitrogen donors of four acetaldoxime molecules in the equatorial plane and two chloride ions in the axial positions. Strong intramolecular hydrogen-bonding interactions from the aldoxime OH to the chloride ions are present (Table 4). Furthermore, the molecules are linked together into a one-dimensional chain by O $\cdots$ O intermolecular hydrogen bonding between the aldoxime OH groups of neighbouring molecules.

The unit cell of the bromide analogue **5** (space group $P2_1/c$) contains two molecules, the asymmetric unit having only half a molecule. The cobalt ion is again in an octahedral geometry formed by the nitrogen donors of four acetaldoxime molecules in the equatorial plane and two bromide ions in the axial

Table 3 Selected bond lengths (Å) and angles (°) for complexes **4** and **5**

4		5	
Co(1)–Cl(1)	2.4427(4)	Co(1)–Br(1)	2.6524(2)
Co(1)–N(1)	2.1711(15)	Co(1)–N(1)	2.157(2)
Co(1)–N(2)	2.1752(14)	Co(1)–N(2)	2.165(2)
Cl(1)–Co(1)–N(1)	87.93(4)	Br(1)–Co(1)–N(1)	88.34(6)
Cl(1)–Co(1)–N(2)	92.12(4)	Br(1)–Co(1)–N(2)	89.22(5)
N(1)–Co(1)–N(2)	89.66(5)	N(1)–Co(1)–N(2)	90.25(7)

Table 4 Hydrogen bonding distances (Å) and angles (°) for complexes **4** and **5**

4		5	
H(1)···Cl(1)	2.26(3)	H(1)···Br(1)	2.55(4)
O(1)···Cl(1)	3.022(2)	O(1)···Br(1)	3.183(2)
H(2)···Cl(1)^a	2.31(3)	H(2)···Br(1)	2.35(4)
O(2)···Cl(1)^a	3.038(2)	O(2)···Br(1)	3.125(3)
O(1)–H(1)···Cl(1)	158(3)	O(1)–H(1)···Br(1)	154(4)
O(2)–H(2)···Cl(1)^a	155(3)	O(2)–H(2)···Br(1)	161(4)
H(1)···O(1)^b	2.55(3)	No intermolecular bonding	
O(1)···O(1)^b	2.843(3)		
O(1)–H(1)···O(1)^b	103(2)		

Symmetry operations: ^{a} $1 - x, -y, -z$; ^{b} $1 - x, 1 - y, -z$.

positions. Intramolecular hydrogen bonding from the aldoxime OH to the bromide ions is present, but in contrast to **4** there are no intermolecular hydrogen-bonding interactions in this compound.

Comparison of the structures

The crystal structure of [Ni(aax)$_4$Cl$_2$] has been reported[10] and compound **5** appears to be structurally isomorphous to it; the two crystallise in the same space group, with near identical unit cell dimensions. Interestingly, it has been reported that the nickel complex is hygroscopic, which is consistent with the observed instability of the cobalt and manganese analogues. The crystal structure of a cobalt(II) chloride complex of furaldehyde oxime has also been described,[2f] unfortunately no detailed synthesis (or yield) was reported. All these structures show several common features: the metal ion resides on an inversion centre and there are intramolecular hydrogen-bonding interactions between the oxime OH and the coordinated halide ion. In this respect, an interesting comparison can also be made with the complex dibromotetrakis(5-methylpyrazole)-manganese in which the metal ion also resides on an inversion centre, and has similar hydrogen-bonding interactions, but now from the pyrazole N–H to the apical bromide ion.[14]

Characterisation of the complexes

The aldoxime complexes are formed quite easily in good yield under anhydrous conditions, by the use of trimethyl orthoformate. Elemental analyses revealed that all compounds are in a 1 : 4 metal to ligand ratio, and have the general formula [M(L)$_4$X$_2$].

The infrared spectra of the butyraldoxime complexes and the two acetaldoxime complexes are mutually very similar. Most prominent in these spectra are the strong O–H stretching band at around 3250 cm^{-1}, and a weak C=N stretching band at 1670 cm^{-1} confirming the presence of the oxime moiety in the complexes. Typical frequencies of these bands for free butyraldoxime are 3240 and 1660 cm^{-1}, respectively.

The X-ray determinations of compounds **1**, **4**, and **5** show that the cobalt ions are in distorted octahedral environments, in which the nitrogen atoms of the aldoxime ligands form the equatorial plane and the halide ions are in the apical positions. From similarities in the infrared spectra of the various compounds and the elemental analyses, there is little doubt that the coordination environments of the cobalt ions in **2** and the manganese ions in **3** are also elongated octahedral.

The ligand field spectra of the four cobalt complexes reveal the prominence of their tetragonal distortion. For a high-spin d^7 cobalt(II) ion in a regular octahedron (O_h) three spin-allowed transitions are to be expected, whereas for d^7 systems in a D_{4h} geometry up to six spin-allowed transitions are possible.[15,16] All cobalt complexes show splitting of the low-energy band due to the tetragonal distortion. This distortion is even more pronounced in the bromide complexes, especially for **5** which shows beautiful doublet resolution on the high-energy bands due to splitting of the triplet ground state $^4T_{1g}$ into $^4A_{2g}$ and ^4E_g levels.

Of the manganese halides, only the complex [Mn(bax)$_4$Cl$_2$] **3** could be isolated and characterised by IR spectroscopy and its melting point. The infrared spectrum is identical to that of the cobalt analogue **1** apart from the position of the OH stretching vibration (3260 and 3300 cm^{-1} for **1** and **3**, respectively). Compound **3** is extremely unstable and rapidly decomposes to the manganese hydrate salt. All compounds lose the oxime ligands and regenerate the starting hydrate in ambient atmosphere, but for the acetaldoxime derivatives this process is not as fast as for the butyraldoxime complexes. These differences are also reflected in the melting points of the compounds. The presence or absence of intermolecular hydrogen-bonding interactions in compounds **4** and **5** also influences the physical properties of the complexes, possibly explaining the differences in melting points for [Co(aax)$_4$Cl$_2$] and [Co(aax)$_4$Br$_2$].

Conclusion

The complexes presented in this work were synthesised with the aim of creating a better understanding of the possible interactions of the constituents of alkyd paints, and to gain insight in their role in the drying mechanism. Initially, attempts were made to synthesise cobalt and manganese carboxylate complexes of butanone oxime and the aldoximes mentioned. Such complexes, however, could not be isolated. The cobalt halide complexes that were obtained with the ligands butyraldoxime and acetaldoxime could be analysed satisfactorily despite their notable instability. Moreover, the manganese complexes appeared to be even less stable and only one of these could be characterised unambiguously. From similarities in the infrared spectra of the various compounds and the elemental analyses there is little doubt that the metal ions in all five complexes have similar geometries. All the complexes are stabilised by intramolecular hydrogen bonding. The extreme instability of the manganese complexes may be attributed to the relatively large ionic radius of the manganese(II) ions, and the resulting weaker hydrogen bonds.

Based on the observations reported it may be concluded that the interactions between the oxime additives and the cobalt drier in alkyd paints are non-existent or at best only very weak. The high instability of the isolated coordination complexes towards atmospheric water and the presence of small amounts (0.5%) of water in solvent-borne alkyds almost certainly preclude the formation of cobalt oxime interactions in paints.

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References

1 See for instance: V. Y. Kukushkin, D. Tudela and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1996, **156**, 333; V. Y. Kukushkin and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1999, **181**, 147; and references therein.

2 (*a*) W. Hieber and F. Leutert, *Chem. Ber.*, 1927, **60**, 2296; (*b*) N. A. Patel, J. R. Shah and R. P. Patel, *Indian J. Chem., Sect. A*, 1980, **19**, 236; (*c*) A. Goldhaber, K. P. C. Vollhardt, E. C. Walborsky and M. Wolfgruber, *J. Am. Chem. Soc.*, 1986, **108**, 516; (*d*) R. C. Mehrotra, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2, pp. 270 and 271 and references therein; (*e*) T. Carofiglio, S. Stella, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1989, 1957; (*f*) B. Norén, Å. Oskarsson, K. C. Dash and M. Mohapatra, *Acta Crystallogr. Sect. C*, 1990, **46**, 2093.

3 L. G. Marzilli, in *Bioinorganic Catalysis*, eds. J. Reedijk and E. Bouwman, Marcel Dekker, New York, 1999.

4 S. T. Warzeska, J. A. P. P. van Dijk, W. Muizebelt, E. Bouwman and J. Reedijk, in preparation.

5 J. Bieleman (Editor), *Additives for Coatings*, Wiley-VCH, Weinheim, 2000.

6 J.-C. Hierso, A. Eikelboom, S. T. Warzeska, E. Bouwman and J. Reedijk, in preparation.

7 J.-C. Hierso, D. D. Ellis, A. L. Spek, E. Bouwman and J. Reedijk, *Chem. Commun.*, 2000, 1359.

8 J.-C. Hierso, D. D. Ellis, A. L. Spek, E. Bouwman and J. Reedijk, *Eur. J. Inorg. Chem.*, 2000, 2459.

9 M. Tanimura, T. Mizushima and Y. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2777; Y. Kitano, K. Kobori, M. Tanimura and Y. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2969; V. Y. Kukushkin, V. K. Belsky, D. Tudela, E. A. Aleksandrova, V. E. Konovalov and G. A. Kirakosyan, *Inorg. Chem.*, 1992, **31**, 3836.

10 M. E. Stone, B. E. Robertson and E. Stanley, *J. Chem. Soc. A*, 1971, 3632.

11 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, DIRDIF 99 Program System, Technical Report, Crystallography Laboratory, University of Nijmegen, 1999.

12 G. M. Sheldrick, SHELXL 97. Program for crystal structure refinement, University of Göttingen, 1997.

13 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, 2000.

14 J. Reedijk, B. A. Stork-Blaisse and G. C. Verschoor, *Inorg. Chem.*, 1971, **10**, 2594.

15 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1986.

16 J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 993.