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FULL PAPER

Diazopyrazolones as weak solvent extractants for copper from ammonia leach solutions†

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Potentially bidentate 4-diazopyrazol-5-one ligands carrying a range of substituents can readily be prepared by coupling arene diazonium salts on to the appropriate pyrazolones. Hydrocarbon-soluble versions are shown to be suitable reagents for the recovery of copper by solvent extraction from ammoniacal leach solutions, and potentially have greater resistance to chemical degradation than the β-diketones which have been used. Cobalt(III), nickel(II), copper(II) and zinc(II) complexes with 4-(4-*tert*-butylphenylazo)-3-methyl-1-phenyl-5-pyrazolone (HL) have been characterised by X-ray crystallography. The significant deviations from planar coordination geometry which are observed in [CuL_2] and [CuL'_2], where HL′ is 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone, arise from interligand repulsion, and account for the relatively weak complexation and ease of stripping of copper from this class of extractant. The cobalt(III) complex [CoL_3]·3MeOH and the high spin nickel(II) complex [$NiL_2(MeOH)_2$]·2MeOH both have approximately octahedral geometries, but show significantly different bite distances in the chelate rings. The zinc complex [ZnL_2] has a pseudo-tetrahedral structure.

Introduction

The economic and environmental benefits of recovering copper by hydrometallurgical, rather than smelting, processes have led to considerable research and development[1–3] of novel leach and extraction processes. A process based on ammoniacal leaching of chalocite-based ores under mild conditions[4–6] generates two copper streams; an enriched ore, covellite, which can be treated in a conventional smelter, and a concentrated aqueous solution (*ca.* 5 M, pH 8.5–10) containing ammine complexes [eqn.)1)]. Solvent extraction with a weakly acidic reagent, as in eqn. (2), regenerates the leachant which is recycled. Stripping the copper from the loaded organic solution with acid (eqn. 3), followed by electrowinning the copper (eqn. 4), regenerates the extractant without overall consumption of acid. The recycling of reagents between the unit operations leads to a remarkable materials balance with the overall process being represented by eqn. (5).

$$\underset{\text{Chalcocite}}{Cu_2S(s)} + 2\,NH_3(aq) + 2[NH_4]^+(aq) + \tfrac{1}{2}O_2(g) \longrightarrow \underset{\text{Covellite}}{CuS(s)} + [Cu(NH_3)_4]^{2+}(aq) + H_2O(l) \qquad (1)$$

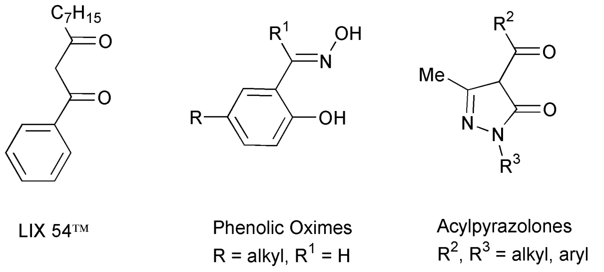
$$[Cu(NH_3)_4]^{2+}(aq) + 2HL(org) \longrightarrow [CuL_2](org) + 2[NH_4]^+(aq) + 2NH_3(aq) \qquad (2)$$

$$[CuL_2](org) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + 2LH(org) \qquad (3)$$

$$CuSO_4(aq) + H_2O(e) \longrightarrow Cu(s) + H_2SO_4(aq) + \tfrac{1}{2}O_2(g) \qquad (4)$$

$$Cu_2S \longrightarrow Cu + CuS \qquad (5)$$

The pH of the lixiviant and the leach conditions employed are such that very little of the iron present in the ores and only small quantities of other transition metals are transferred to the pregnant leach solution (pls).[7] As a consequence, and in marked contrast to the well established acid leach process,[8] the solvent extractant used to recover the copper is not required to show very high selectivity for copper over iron or high "strength" because the extraction equilibrium [eqn. (2)] is effectively buffered by $[NH_4]^+/NH_3$. Henkel's LIX54™ reagent, 1-heptyl-3-phenyl-1,3-propanedione (mixed isomer heptyl substituent, Fig. 1), provides "strength" and selectivity well suited to ammoniacal recovery processes. However, a potential problem with organic reagents which contain reactive carbonyl groups is their propensity to form the corresponding imines in contact with the high levels of NH_3 present in the pregnant leach solution. Apart from the potential loss of the active reagent from the system, these imines may also contribute to poor phase disengagement which will in turn lead to high entrainment of the aqueous phase in the loaded organic. For these reasons other systems are now being considered.[9,10]



LIX 54™

Phenolic Oximes
R = alkyl, R^1 = H

Acylpyrazolones
R^2, R^3 = alkyl, aryl

Fig. 1 Structures of commercial metal extractants and acylpyrazolones.

Acylpyrazolones (Fig. 1) also form neutral β-diketonate-type complexes suitable for extraction of a range of metals into organic solvents[11–16] and have been considered[17] as alternatives to LIX54™ for use in ammoniacal leach circuits. Although they are stronger copper extractants than LIX54™, the low solubility of their metal complexes limits[18] their usefulness. The structurally related diazopyrazolones (Scheme 1) have not previously been investigated as copper extractants, but possess very well

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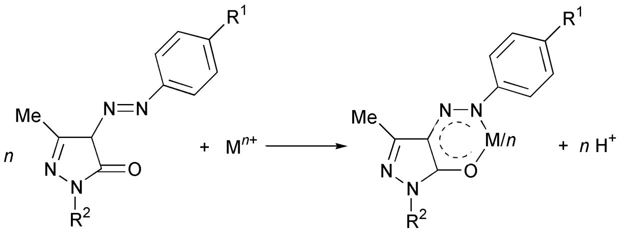
† Electronic supplementary information (ESI) available: characterisation data for compounds **2**–**7** and complexes **13**–**15**, bite angles/distances in the complexes and deviations from planarity of **1**, **2** in the complexes. See http://www.rsc.org/suppdata/dt/b1/b101780m/



Ligands	R^1	R^2	Complexes	
1	*t*-Bu	Ph	8	[Cu(**1**-H)$_2$]
2	H	Ph	9	[Zn(**1**-H)$_2$]
3	*t*-Bu	H	10	[Co(**1**-H)$_3$]•3MeOH
4	*t*-Bu	Me	11	[Ni(**1**-H)$_2$(MeOH)$_2$]•2MeOH
5	*t*-Bu	*t*-Bu	12	[Cu(**2**-H)$_2$]
6	*s*-Bu	*t*-Bu	13	[Cu(**5**-H)$_2$]
7	nonyl	*t*-Bu	14	[Cu(**6**-H)$_2$]
			15	[Cu(**7**-H)$_2$]

Scheme 1 Formation of complexes of diazopyrazolones.

defined synthetic chemistry[17] due to their extensive use in the dyestuffs industry.[19] They have been shown[20,21] to form neutral 2 : 1 complexes with copper (Scheme 1) with an $N_2O_2^{2-}$ donor set analogous to that in the commercially successful phenolic oxime extractants (Fig. 1) used to recover copper from acidic leach solutions.[8] In this paper we report the coordination chemistry and extraction properties of a series of diazopyrazolones with a range of first row transition metals.

Experimental

Instrumentation

IR spectra were obtained on a Perkin-Elmer Paragon 1000 FT-IR spectrometer as potassium bromide discs or as liquid thin films. ^{1}H and ^{13}C NMR spectra were run on Bruker WP200, AC250 and DPX300 spectrometers and NOE experiments on a Bruker WH360 spectrometer. Electron impact (EI) mass spectra were obtained either on a Finnigan MAT4600 quadrupole spectrometer or on a Kratos MS50TC spectrometer and fast atom bombardment (FAB) mass spectra on a Kratos MS50TC spectrometer in acetonitrile/3-nitrobenzyl alcohol matrices. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed on a Thermo Jarrell Ash IRIS ICP-AES spectrometer. Magnetic susceptibilities were measured for the paramagnetic complexes **8**, **11**, **12**, **13**, and **14** using the Evans NMR method[22,23] or a Johnson Matthey magnetic susceptibility balance and molar susceptibilities were corrected for diamagnetism using Pascal's constants.[24]

Solvent and reagent pretreatment

Substituted anilines and pyrazolones were commercially available (Acros or Aldrich) with the exception of 1,3-dimethyl-5-pyrazolone and 1-*tert*-butyl-3-methyl-5-pyrazolone, which were prepared by the method of Butler and DeWald.[25] Solvents used for analytical purposes (NMR, MS) were of spectroscopic grade. Deuteriated dimethyl sulfoxide for use in NOE experiments was dried over 4 Å molecular sieves under nitrogen. All other reagents and solvents were used as received.

Synthesis of the ligands

Compounds **1**–**7** were prepared as described for **1** by diazotisation of the reagent grade anilines and coupling[13] with the appropriate pyrazolones.

4-(4-*tert*-Butylphenylazo)-3-methyl-1-phenyl-5-pyrazolone 1. Aqueous sodium nitrite (2 M, 10 ml) was added to a stirred solution of 4-*tert*-butylaniline (2.98 g, 20 mmol) in water (20 ml) containing concentrated hydrochloric acid (4 ml, 40 mmol) at 0–5 °C. After 1 h this was added to a solution of 3-methyl-1-phenyl-5-pyrazolone (3.48 g, 20 mmol) in acetone (40 ml) and water (40 ml) at 0–5 °C. Addition of sodium acetate (10 g, 120 mmol) yielded a bright orange suspension, which was stirred for 2 h at 0–5 °C, collected by filtration, washed with water and recrystallised (methanol–water, 20 : 1) to yield **1** (5.34 g, 66%) as orange needles; mp 138–139 °C (Found C, 71.8; H, 6.75; N, 17.0. $C_{20}H_{22}N_4O$ requires C, 71.8; H, 6.6; N, 16.8%). IR (cm^{-1}, KBr disc): ν 3430m (NH), 1654s (C=O), 1551s (C=N). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 1.32 (s, 9H, C(CH$_3$)$_3$), 2.36 (s, 3H, CH$_3$), 7.15–7.24 (tt, J_{ortho} 7.41, J_{meta} 1.87, 1H, *p*-H of Ph), 7.34–7.47 (m, J_{ortho} 6.34 Hz, 4H (Ar*H*–N=N) and 2H (*m*-H of Ph)), 7.91–7.98 (dd, J_{ortho} 7.58, J_{meta} 2.11 Hz, 2H, *o*-H of Ph), 13.62 (br s, 1H, NH). ^{13}C NMR (CDCl$_3$, 63 MHz): δ 11.71 (CH$_3$), 31.20 (C(*C*H$_3$)$_3$), 34.52 (*C*(CH$_3$)$_3$), 115.51 (aryl), 118.48 (aryl), 125.00 (aryl), 126.47 (aryl), 127.88 (aryl), 128.81 (aryl), 137.97 (aryl), 138.59 (aryl), 148.46 (C=N–NH), 149.19 ([CH$_3$]*C*=N, ring), 157.75 (C=O). EIMS: *m*/*z* 334 (70.0, M$^+$), 319 (100.0, M − CH$_3$), 132 (14.1, (CH$_3$)$_3$CPh), 91 (20.0, PhN), 77 (34.9%, Ph).

Ligands **2**–**7** were prepared similarly. Yields and characterisation data are provided in ESI supplementary material.

Complexes

[Cu(1 − H)$_2$] 8. Copper(II) nitrate trihydrate (0.242 g, 1 mmol) in methanol (15 ml) was added to **1** (0.668 g, 2 mmol) in methanol (40 ml) containing potassium hydroxide (0.112 g, 2.00 mmol). The resulting dark brown solution was stirred for 0.5 h at room temperature to afford a dark black/brown precipitate, which was recrystallised (methanol–acetone, 3 : 1) to yield dark red crystals of [Cu(**1** − H)$_2$] (0.528 g, 72%); mp 238–240 °C (Found C, 65.5; H, 5.9; N, 15.4. $C_{40}H_{42}CuN_8O_2$ requires C, 65.8; H, 5.8; N, 15.3%). IR (cm^{-1}, KBr disc): ν 1561s (C=N), 1414m and 1367m (C(CH$_3$)$_3$). FABMS: *m*/*z* 858 (28.9, Cu$_2$L$_3$), 794 (29.2, Cu$_2$L$_2$), 730 (13.2, CuL$_2$), 461 (32.0, Cu$_2$L), 397 (41.1, CuL), 334 (38.5, L), 133 (100.0, (CH$_3$)$_3$CPh), 63 (89.9%, Cu). $\mu_{eff} = 1.8\ \mu_B$ (Evans).

[Zn(1 − H)$_2$] 9. Zinc(II) acetate dihydrate (0.079 g, 0.36 mmol) was added to **1** (0.701 g, 2.1 mmol) in methanol (20 ml) containing triethylamine (1 ml, 7.17 mmol). The resulting pale yellow solution was stirred for 0.5 h at room temperature to yield pale yellow crystals of [Zn(**1** − H)$_2$] (0.193 g, 75%); mp 233–235 °C (Found C, 64.1; H, 5.9; N, 15.2; $C_{40}H_{42}N_8O_2$-Zn·H$_2$O requires C, 64.0; H, 5.9; N, 14.9%). IR (cm^{-1}, KBr disc): ν 1549s (C=N), 1413s and 1365m (C(CH$_3$)$_3$). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 1.27 (s, 18H, 2 C(C*H*$_3$)$_3$), 2.54 (s, 6H, 2 C*H*$_3$), 7.15–7.47 (m, 8H, Ar*H*–N=N and 6H(Ph)), 7.47–7.99 (m, 4H, *o*-H of Ph). FABMS: *m*/*z* 731 (100.0, ZnL$_2$), 334 (42.7%, L).

[Co(1 − H)$_3$]·3MeOH 10. Cobalt(II) acetate tetrahydrate (0.087 g, 0.35 mmol) was added to **1** (0.701 g, 2.10 mmol) in methanol (20 ml). The resulting dark orange solution was stirred for 0.5 h at room temperature to yield red crystals of [Co(**1** − H)$_3$]·3MeOH (0.241 g, 60%); mp 212–213 °C (Found C, 67.7; H, 6.1; N, 15.4. $C_{60}H_{63}CoN_{12}O_3$ requires C, 68.0; H, 6.0; N, 15.9%). IR (cm^{-1}, KBr disc): ν 1556s (C=N), 756s (ArH). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.95 (s, 9H, C(C*H*$_3$)$_3$), 1.17 (s, 9H, C(C*H*$_3$)$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$), 1.99 (s, 3H, C*H*$_3$), 2.33 (s, 3H, C*H*$_3$), 2.59 (s, 3H, C*H*$_3$); 6.37–6.42 (d, 2H), 6.86 (s, 4H), 6.98–7.33 (m, 18H), 7.45–7.53 (t, 2H), 8.04–8.09 (d, 1H) (all Ar*H*). FABMS: *m*/*z* 725 (100.0, CoL$_2$), 525 (8.6, CoL + (CH$_3$)$_3$CPh), 133 (9.0%, (CH$_3$)$_3$CPh).

[Ni(1 − H)$_2$(MeOH)$_2$]·2MeOH 11. Nickel(II) acetate tetrahydrate (0.087 g, 0.35 mmol) was added to **1** (0.701 g, 2.10 mmol) in methanol (20 ml). The resulting dark orange solution was stirred for 0.5 h at room temperature to yield red crystals of [Ni(**1** − H)$_2$(MeOH)$_2$]·2MeOH (0.168 g, 61%); mp 245–247 °C (Found C, 64.4; H, 6.2; N, 14.7. $C_{40}H_{42}N_8NiO_2$·H$_2$O requires C,

Table 1 Crystallographic data for complexes **8**–**12**

	8	**9**	**10**[a]	**11**	**12**
Formula	$C_{40}H_{42}N_8CuO_2$	$C_{40}H_{42}N_8O_2Zn$	$C_{60}H_{63}CoN_{12}O_3\cdot 3MeOH$	$C_{42}H_{42}N_8NiO_2\cdot 2MeOH$	$C_{32}H_{26}N_8CuO_2$
M	730.36	732.19	115.28	853.69	618.15
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic twin
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.603(3)	12.280(5)	12.965(6)	10.5849(12)	8.307(4)
b/Å	23.586(4)	13.615(5)	15.604(6)	14.8955(17)	11.311(6)
c/Å	13.649(2)	14.172(5)	15.584(6)	15.1532(17)	16.415(8)
α/°		113.74(2)	75.83(3)	76.735(6)	75.87(4)
β/°	97.24(2)	95.13(2)	85.67(3)	79.025(6)	75.79(4)
γ/°		113.635(14)	86.50(4)	77.539(7)	71.58(4)
U/Å^3	3705.5(13)	1896.2(12)	3045(2)	2245.6(4)	1395.1(12)
Z	4	2	2	2	2
μ/mm^{-1}	1.197	1.256	0.342	1.065	1.485
No. of unique data	5435	6746	10736	7969	3946
No. data with $[F > \sigma(F)]$	4000	5713	5472	6601	3098
$R1$	0.0614	0.0342	0.0846	0.0389	0.0504
$wR2$	0.1732	0.1002	0.2201	0.1042	0.1753

[a] This unit cell may be transformed into a pseudo *C*-centred monoclinic cell by the matrix (011/01 − 1/ − 100), but R_{int} for 2/*m* Laue symmetry was 64%.

64.6; H, 6.0; N, 15.1%). IR (cm^{-1}, KBr disc): *ν* 1581s (C=N), 755s (ArH). FABMS: *m*/*z* 725 (100.0, NiL_2), 393 (16.9, NiL), 334 (74.2, L), 257 (8.1, L − Ph), 133 (66.2, $(CH_3)_3CPh$), 91 (71.1, PhN), 57 (85.9%, $C(CH_3)_3$); $\mu_{eff} = 2.7\ \mu_B$ (Evans).

Complexes **12**–**15** were prepared as described for **12** by reaction of two equivalents of the appropriate diazopyrazolone ligand with one equivalent of copper(II) acetate monohydrate in methanol.

[Cu(2 − H)₂] 12. Copper(II) acetate monohydrate (0.100 g, 0.5 mmol) was added to **2** (0.278 g, 1 mmol) in methanol (25 ml). The resulting red solution afforded a red/brown powder, [Cu(**2** − H)$_2$]·2MeOH (0.277 g, 90%). FABMS: *m*/*z* 682 ([Cu(**2** − H)$_2$]·2MeOH). This was recrystallised by diffusion of water into a DMF solution of the complex to yield red crystals, [Cu(**2** − H)$_2$], mp 220–222 °C (Found C, 61.8; H, 4.1; N, 18.1. $C_{32}H_{26}CuN_8O_2$ requires C, 62.2; H, 4.25; N, 18.1%). IR (cm^{-1}, KBr disc): *ν* 1564s (C=N), 1394w and 1364m ($C(CH_3)_3$). FABMS: *m*/*z* 1300 (7.0, Cu_3L_4), 1022 (4.0, Cu_3L_3), 745 (13.8, Cu_3L_2), 681 (14.8, Cu_2L_2), 618 (55.6, CuL_2), 340 (17.9, CuL), 77 (40.5%, Ph). $\mu_{eff} = 1.80\ \mu_B$ (Balance).

Yields and characterisation data for **13**–**15** are provided as ESI.

Crystallography

In all cases data were collected at 220 K on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device, using Cu-Kα radiation for **8**, **9**, **11** and **12**, and Mo-Kα radiation for **10**. Structures **8** and **12** were solved by direct methods (SHELXTL or SIR 92)[26,27] and **9**–**11** by Patterson methods (DIRDIF).[28] All were completed by iterative cycles of least-squares refinement against F^2 and Fourier difference syntheses (SHELXTL). H atoms were idealised, those belonging to CH_3 groups being first located in a difference synthesis. In all cases all non-H atoms were modelled with anisotropic displacement parameters and final refinement statistics are presented in Table 1.

Crystals of **12** grew as aggregates of blocks, and none of the crystals studied was single. In the case of the sample from which data are reported here a random reflection search located 25 reflections. This pattern was completely indexed on the basis of two orientation matrices.[29] Some reflections in the search list gave integral indices with only one of these matrices, others could be satisfactorily indexed with both. Data were collected as described above using one of these matrices; no absorption correction was applied. Routine refinement converged to $R1 = 6.75\%$ with a difference synthesis extrema of 1.13 and −0.74 e Å^{-3}.

The relationship between the two orientation matrices identified after the initial reflection search can be expressed by the matrix[30] shown. Several twinning models were considered,

$$\begin{pmatrix} 0.01 & -0.414 & 0.50 \\ 0 & -1 & 0 \\ 2.03 & -0.815 & 0.01 \end{pmatrix}$$

including splitting relections with $k = 5n$ and $l = 2n$, but with only slight improvement. In all cases the twin scale factor was less than 10%. It is possible that the off-diagonal terms in this matrix are far enough from rational numbers that the scan path taken during data collection meant that the twinning did not affect the intensity measurements in a consistent manner. The best agreement indices were obtained when all reflections whose transformed indices differed from integral values by less than 0.15 were omitted (603 data in all). *R*1 under these conditions was 5.04%. Other refinement details are given in Table 1.

CCDC reference numbers 158372–158376.

See http://www.rsc.org/suppdata/dt/b1/b101780m/ for crystallographic data in CIF or other electronic format.

Results and discussion

Preparation of the ligands

The free ligands **1**–**7** were readily prepared by coupling the appropriate pyrazolone and diazonium salt derived from the appropriate *para*-substituted aniline. All are highly coloured (yellow/orange), as might be expected, because diazopyrazolones have been used[19] extensively for over a century in the dyestuffs industry. Ligands **1**–**4** with N-phenyl, N-methyl and unsubstituted pyrazolone units are solids which are easily recrystallised and characterised, but their solubilities and those of their copper(II) complexes in hydrocarbon solvents were judged to be too low to carry out effective solvent extraction measurements. Incorporation of a *t*-butyl group on the pyrazolone and a branched alkyl group in the *para* position of the phenylazo group gave ligands **5**–**7**, with much higher hydrocarbon solubility, but which could only be isolated as viscous oils.

^{1}H and ^{13}C NMR spectra are consistent with the structures **1**–**7**, and NOESY experiments carried out on **1** indicate that this exists in the hydrazone form (Fig. 2: A) in deuteriated chloroform or dimethyl sulfoxide. ^{15}N NMR experiments carried out by Connor *et al.*[30] and crystal structure determination[30–37] support the formulation of arylazopyrazolones

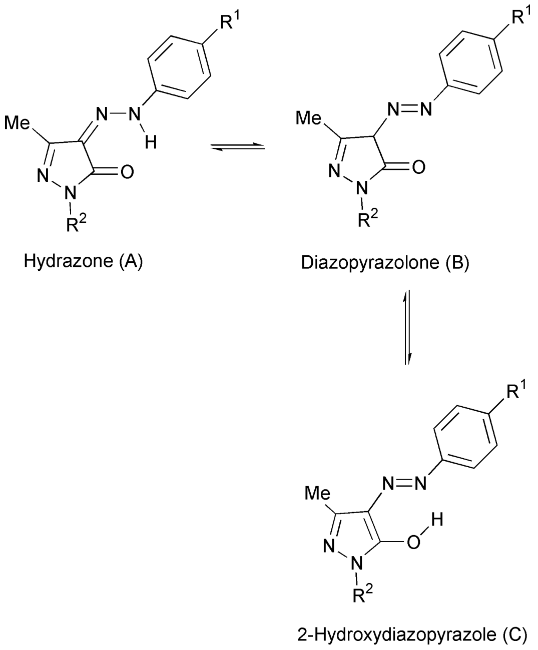


Fig. 2 Tautomeric forms of diazopyrazolones.

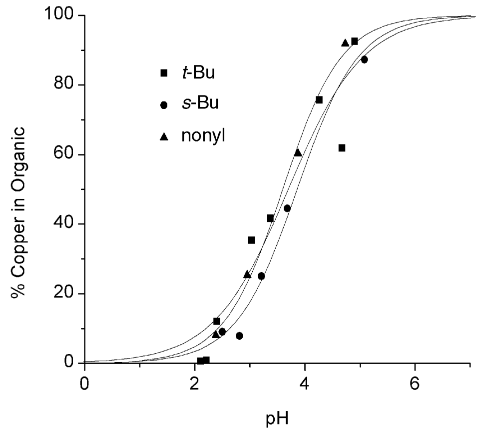


Fig. 3 S-Curves for the extraction of copper by the ligands **5**–**7** (R^1 = *t*-Bu and R^2 is varied as indicated, see also Scheme 1).

as their hydrazone tautomers, both in solution and the solid state.

Metal complexes

Infrared bands at *ca.* 1650 and 3400 cm^{-1} associated with the keto–hydrazone tautomers of the ligands are lost on formation of the metal complexes (**8**–**15**, Scheme 1). The FAB mass spectra for the complexes all show molecular ions associated with the neutral ML_2 or ML_3 complexes. In addition, the copper complexes **8** and **12** show lower intensity high mass peaks attributed to Cu_2L_3 and Cu_2L_2 for **8** and Cu_3L_4, Cu_3L_3 and Cu_2L_2 for **12**. In view of the satisfactory analytical data obtained for these compounds, it is assumed these species are produced in the mass spectrometer.

The colour changes associated with complex formation can be used to monitor the displacement of metals from the ligand in solvent extraction experiments (*vide infra*).

Solvent extraction

The strength of extractants that operate on a “pH-swing” controlled process of the type shown in eqn. (2) can be assessed by determining their $\mathrm{pH}_{\frac{1}{2}}$ values (the pH values associated with 50% theoretical loading of a particular metal). Their $\mathrm{pH}_{\frac{1}{2}}$ values (Fig. 3) of *ca.* 3.7 are higher than those for the “strong” phenolic oxime extractants (Fig. 1), used[8] commercially for the recovery of copper from acid sulfate leach solutions, but are almost ideal for the Escondida-type circuit. Good loading will result from the $[NH_4^+]/NH_3$ buffered feed solution, whilst almost quantitative stripping is expected when using spent tankhouse electrolyte (pH 0–0.5).

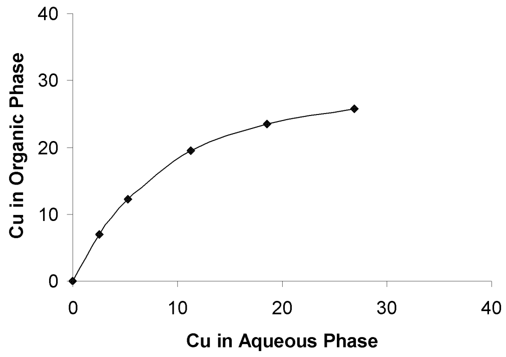


Fig. 4 Extraction isotherm for azopyrazolone **7** contacted with 30 g l^{-1} copper feed (copper values all g l^{-1}).

S-Curves of the type shown in Fig. 3 can also be used[9] to assess the selectivity of metal extraction. The $\mathrm{pH}_{\frac{1}{2}}$ values, Cu 4.7, Zn 5.8 and Ni > 7.0, are consistent with selectivities which follow the Irving–Williams order of complex stabilities, but with the nickel(II) complex formation being more disfavoured than normal relative to zinc. Reproducibility of extraction of cobalt was poor and the results were consistent with extraction of cobalt(II) and subsequent oxidation to cobalt(III) *(vide infra)*. Such oxidation is likely to make stripping difficult on both thermodynamic and kinetic grounds. However, the potential poisoning of the extractant by cobalt in an Escondida-type circuit is unlikely to be a problem in practice because the ore bodies do not contain any significant levels of cobalt. The strength of the azopyrazolones as copper extractants from ammoniacal feeds is shown in Fig. 4 which presents the equilibrium extraction isotherm for a 1.0 M solution of **7** in Philips Orfom SX7® diluent after contact at 20 °C with an aqueous copper feed containing Cu 30, SO_4^{2-} 75 and NH_3 45 g l^{-1} at various aqueous to organic ratios (A : O). The copper contents of the aqueous and organic phases for each A : O ratio were determined using atomic absorption spectroscopy.

Stripping of the loaded organic phase of **7** with simulated spent tankhouse electrolyte containing 30 g l^{-1} copper and 180 g l^{-1} sulfuric acid was found to be virtually quantitative. Fig. 5 shows equilibrium isotherms for **7** with McCabe–Thiele[38] constructions for the recovery of copper from a 30 g l^{-1} copper feed and stripping with 30 g l^{-1} copper and 180 g l^{-1} sulfuric acid. The McCabe–Thiele data were modelled for a process based on 2 stages of extraction and 2 stages of stripping and assuming 90 and 95% stage efficiencies in extraction and stripping respectively. The computed model indicates that copper recoveries in excess of 93% may be expected, while producing a regenerated electrolyte containing 45 g l^{-1} copper from which the copper metal value may then be recovered in a conventional electrowinning process.

The stability of the solvent extractant to the basic conditions of the Escondida process is of paramount importance. A preliminary assessment of the robustness of the diazopyrazolone **5** was performed by contacting separate samples of a 0.056 M solution of **5** in toluene with equal volumes of 34 and 3.4 g l^{-1} (19 and 1 × excess of copper) ammoniacal copper feeds at room temperature over a period of 23 days. Analysis of both the aqueous and organic phases using ICP-AES showed that, within experimental error, the amount of copper extracted did not decrease over this time period, demonstrating that the ligand does not undergo chemical degradation and is stable to prolonged contact with ammoniacal feeds.

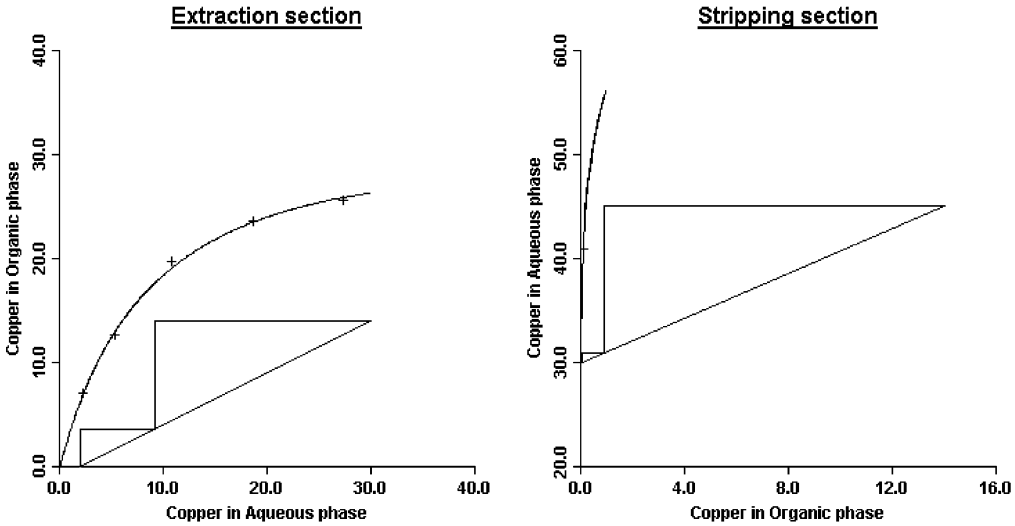


Fig. 5 McCabe–Thiele constructions for the recovery of copper with **7** (1.0 M in Orfom SX7®). All scales in g l^{-1}.

Table 2 Selected bond lengths (Å) in the chelate rings of the complexes of **1**

	Co	Ni	Cu[a]	Zn
M–O5A	1.909(4)	2.0126(13)	1.930(3)	1.9394(14)
M–O5B	1.898(4)	2.0164(13)	1.928(3)	1.9483(14)
M–N42A	1.962(4)	2.0877(17)	1.972(3)	2.028(2)
M–N42B	1.954(5)	2.0824(17)	1.974(3)	2.009(2)
M–X	1.980(5)[b]	2.1017(15)[d]	—	—
	1.959(4)[c]	2.1269(14)[d]	—	—
C4A–N41A	1.335(7)	1.359(2)	1.344(5)	1.340(2)
C4B–N41B	1.342(7)	1.358(2)	1.337(5)	1.347(3)
C4C–N41C	1.345(7)	—	—	—
N41A–N42A	1.269(6)	1.283(2)	1.294(4)	1.297(2)
N41B–N42B	1.301(6)	1.284(2)	1.311(5)	1.293(2)
N41C–N42C	1.285(6)	—	—	—

[a] Similar values were found in the copper(II) complex of **2**: Cu–O 1.935(3), Cu–O 1.920(3), Cu–N 2.000(4), and Cu–N 1.994(4) Å. [b,c] Values for the third diazopyrazolone donors O5C and N42C. [d] Values for the coordinated methanol atoms O1N and O1M.

A series of crystal structure determinations was carried out in an attempt to define why the azopyrazolones are significantly weaker complexing agents than the structurally related phenolic oximes. The copper complexes of both **1** and **2** show small, but significant, deviations from planarity with the O, N, Cu planes associated with the bidentate ligands inclined at 22.7 and 18.4° respectively (Fig. 6). The zinc(II) complex of **1** is pseudo-tetrahedral with the chelate planes inclined at 80.7°, while the nickel complex is pseudo-octahedral with two *cis*-methanol molecules and the two azopyrazolone chelates approximately mutually perpendicular with the oxygen atoms *trans* to each other (Fig. 6). The cobalt complex separates under these conditions as the trivalent pseudo-octahedral complex in which the three azopyrazolone chelates have a *mer, mer* arrangement of their three oxygen and three nitrogen donors. As might be expected bond lengths in the coordination spheres are shortest for low spin cobalt(III), and longest for high spin nickel(II), see Table 2. In each complex the azopyrazolone nitrogen to metal bonds are longer than the oxygen to metal bonds.

The formation of metal complexes is accompanied by significant changes in bond lengths of the diazopyrazolone component of the chelate ring. The N–N bonds (Table 2) are all significantly shorter than those found[30–37] in six uncomplexed diazopyrazolones [mean 1.317(5) Å], whilst the C–N (pyrazolone ring to azo group) bonds are longer than those in the free ligands [mean 1.308(4) Å]. These changes are consistent with the deprotonation and complexation of the hydrazone tautomer (Fig. 2: A) leading to the more delocalised system shown in Scheme 1.

The fused heterocycle and the conjugation in the chelate ring restrict the N···O bites that can be offered to the various metal ions. The largest bite distances and angles (Table 1 of ESI supplementary material), in the zinc complex, are significantly smaller than those required to approach a tetrahedral geometry, while those for the other metals are significantly greater than ideal values for orthogonal coordination sites in these metals. The bite angles in [Co(**1** − H)$_3$] are large because the covalent radius of low spin Co(III) is smaller than for the other metals and in order to achieve the shorter Co–N and Co–O bonds (Table 1 of ESI) the metal ion is located closer to the centroid of the chelate ring.

The coordination of more than one diazopyrazolone unit to a metal centre may result in ligand–ligand contacts that significantly influence their planarity and consequently the conjugation between the aromatic groups. The pseudo-tetrahedral arrangement favoured by divalent zinc allows the maximum separation between the bulky *t*-butylphenyl group and the N-phenyl substituent on neighbouring ligands. As a consequence the phenyl rings are more nearly coplanar with the best plane through the pyrazolone and chelate ring (Table 2 of ESI), and the torsion angles on the diazo bond are close to 180°. The patterns of distortion of the diazopyrazolone ligand are more complicated in the tris complex [Co(**1** − H)$_3$] and in the *cis*-octahedral complex, [Ni(**1** − H)$_2$(MeOH)$_2$], although in all cases the configuration about the diazo bond remains close to planar (Table 2 of ESI), presumably because the most stable form of the six-membered chelate ring is close to planar.

Inter-ligand repulsion terms will have a significant influence on the stability of the copper complexes. In all structures of the 1 : 2 complexes with the "strong" phenolic oxime ligands (Fig. 1) the $N_2O_2^{2-}$ donor set is planar.[39–43] In all but one case[41] the copper atom is located on an inversion centre and the CuN_2O_2 unit is therefore perfectly planar. Planarity is also observed in all four-coordinate copper(II) complexes of unhindered bidentate salicylaldimine ligands[36] (Fig. 7, Table 3).

In contrast, the azopyrazolone complexes **8** and **12** show significant "tetrahedral" distortions that can be ascribed to unfavourable contacts between the azo-phenyl group and the pyrazolyl-phenyl substituent on neighbouring ligands. The closest contact between the ligands in **12** is 2.77 Å between H13A (on the pyrazolone N-phenyl ring) and H48B (on the azo phenyl ring), and between H50A (of the *p*-*t*-butyl group) and H15B (on the N-phenyl ring). Even though the *t*-butyl group is a *para* substituent on the phenylazo unit and is far removed

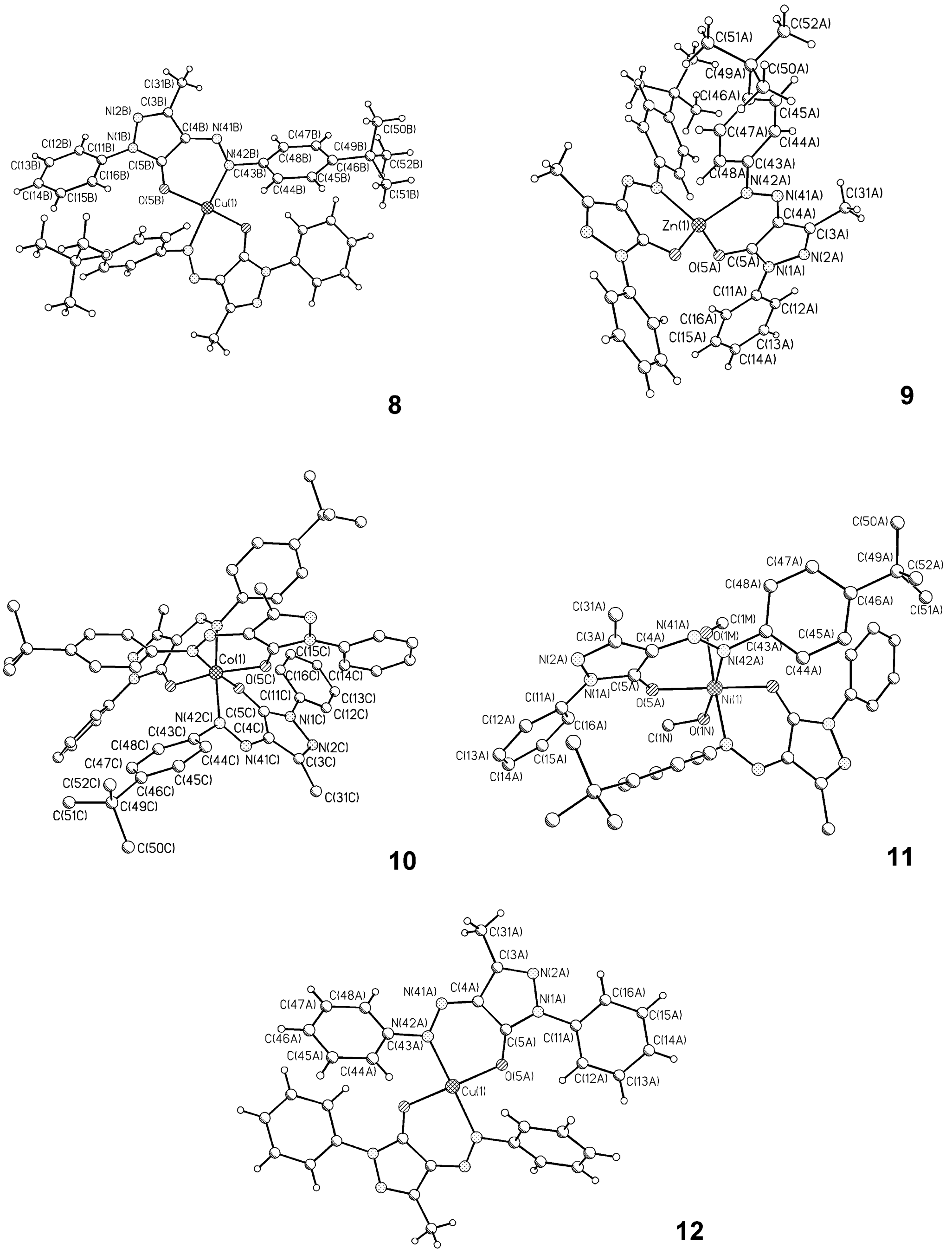


Fig. 6 Structures of the complexes [Cu(**1** − H)$_2$] **8** , [Zn(**1** − H)$_2$] **9**, [Co(**1** − H)$_3$]·3MeOH **10**, [Ni(**1** − H)$_2$(MeOH)$_2$]·2MeOH **11**, and [Cu(**2** − H)$_2$] **12**, showing atom labelling schemes used in the tables. Hydrogens and non-coordinated methanol molecules in **10** and **11** have been omitted for clarity.

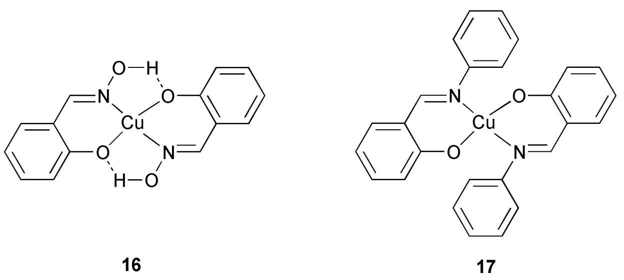


Fig. 7 The pseudomacrocyclic structure of the copper complexes of phenolic oximes, **16**, contrasting with a related salicylaldimine complex, **17**.

from the copper atom it has a significant influence on the metal centre and accounts for the deviation from planarity being greater in **8** than in **12** (see Table 2 of ESI), prising the ligands apart and increasing the dihedral angle between the chelate rings by almost 5°.

The structural studies imply that it is the bulk of the pendant groups in the pyrazolone ligands which underlies the relative weakness of these as extractants for copper(II), making it difficult for 2 : 1 complexes to assume a planar structure. The planar $N_2O_2^{2-}$ donor set preferred by copper(II) is much more readily provided by the phenolic oxime ligands which form the intramolecular hydrogen-bonded pseudomacrocyclic unit shown in Fig. 7. In contrast to the azopyrazolones, these interligand contacts *favour* the presentation of a planar donor set to the complexed metal ion.

Conclusion

Azopyrazolone ligands of the types described above are good candidates for extractants to recover copper from ammoniacal

Table 3 Deviations from planarity[a] of the $N_2O_2^{2-}$ donor sets in the copper(II) complexes of **1** and **2** and related bidentate ligands

	$[\mathrm{Cu}(\mathbf{1}-\mathrm{H})_2]$	$[\mathrm{Cu}(\mathbf{2}-\mathrm{H})_2]$	$[\mathrm{Cu}(\mathbf{16}-\mathrm{H})_2]^b$	$[\mathrm{Cu}(\mathbf{17}-\mathrm{H})_2]^c$
Cu	0.014	0.013	0	0
N	0.277	0.223	0	0
N	0.273	0.223	0	0
O	−0.282	−0.231	0	0
O	−0.282	−0.229	0	0

[a] Distances/Å from the best plane through the CuN_2O_2 unit. [b] Mean displacement/Å for examples[39–43] of phenolic oxime ligands (Fig. 1, R^1 = H, R = H, Cl or ^{t}Bu). [c] Mean displacement/Å for examples[44] of aniline salicylaldimine ligand **17**.

pregnant leach solutions. Good copper transfer efficiency can be obtained; they are relatively weak extractants and are very effiiciently stripped by acidic spent tankhouse electrolyte, whilst the buffering effect of the ammoniacal feed solution ensures good loading of copper into the organic phase in the extract stages. They appear to be more resistant to chemical degradation than β-diketone ligands. One feature, which may restrict their commercialisation, is their intense colours and good dyeing properties. Careful handling on a plant will be needed to prevent staining.

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