Formation and Dissociation of Tetrahedral Nickel(II) and Cobalt(II) Complexes of 'Dithioimidodiphosphato' Ligands, Measurement of Kinetically Determined Stability Constants, and Kinetic Investigations of the Rapid Formation of Tetrahedral Bis(ligand)copper(II) Complexes and Their Rates of Reduction to Trinuclear Copper(I) Species

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Dedicated to Professor *André E. Merbach* in honor of his retirement

The stopped-flow technique was used to measure the rates of formation and dissociation of tetrahedral $[ML_2]$ complexes ($M^{2+} = Ni^{2+}$ or Co^{2+}) of four bidentate S_2-donor 'dithioimidodiphosphato' ligands L^- (HL = $[R^1R^2P(=S)]NH[P(=S)R^3R^4]$, R^1 to R^4 = alkyl) at 25.0° in MeOH/H$_2$O 95 : 5 (*v*/*v*) solution and in the presence of either MOPS (= 3-(morpholin-4-yl)propane-1-sulfonic acid) or 2,6-lutidine (= 2,6-dimethylpyridine) buffers. The kinetically determined equilibrium formation constants for $[ML]^+$ ions (M = Ni or Co) are $10^{-5}\,K = 0.50 \pm 0.01$ or 1.64 ± 0.07 l mol^{-1} for $L = L^3$ ($R^1 = R^2 = Me(CH_2)_2CH(Me)$, $R^3 = R^4 = Me_2CH$), 1.27 ± 0.02 or 7.93 ± 0.09 l mol^{-1} for $L = L^7$ (R^1 to $R^4 = Me_2CHCH_2$), 0.88 ± 0.04 or 3.84 ± 0.13 l mol^{-1} for $L = L^8$ (R^1 to $R^4 = Me_2CH$), and in case of Ni^{2+} 1.88 ± 0.04 l mol^{-1} for $L = L^6$ ($R^1 = R^3 = Bu$, $R^2 = R^4 = {}^tBu$) (see *Table 3*; for L^3 and L^6–L^8, see *Table 1*). Whereas the tetrahedral Ni^{2+} complexes dissociate more slowly than the analogous Co^{2+} species, in all cases, the Co^{2+} complexes are more stable than those of Ni^{2+} due to their larger formation rate constants (*Table 3*). Reactions of Cu^{2+} with eight ligands HL (R^1 to R^4 = alkyl, alkoxy, aryl, and aryloxy) show that formation of intensely colored tetrahedral $[Cu^{II}L_2]$ species is too fast be measured with the available stopped-flow apparatus ($t_{1/2} < 2$ ms), but the subsequent rates of reduction of $[Cu^{II}L_2]$ to give trinuclear products $[Cu^I_3L_3]$ are measurable. An X-ray analysis establishes the structure of one of the $[Cu_3L_3]$ complexes, where $R^1 = R^2 = Me_2CHO$ and $R^3 = R^4$ = 2-(*tert*-butyl)phenyl ($L = L^5$), and a multiwavelength stopped-flow kinetic experiment establishes the spectrum of a tetrahedral $[Cu^{II}L_2]$ species prior to the reduction reactions. The redox reactions proceed at 25.0° with first-order rate constants in the range 0.285 s^{-1} (R^1 to R^4 = PhO; $L = L^{11}$) to $2.58 \cdot 10^{-4}$ s^{-1} (R^1 to $R^4 = Me_2CHCH_2$; $L = L^7$) (*Table 4*).

Introduction. – Ligands HL **1** of the type $(S{=}PR_2)_2NH$ (R = alkyl, alkoxy, aryl, aryloxy)[1]are versatile chelating S_2-donors with the ability to form inorganic (C-free) six-membered M(SPNPS) chelate rings with both main-group and transition metal ions M [1–30]. A review of such systems has appeared [19]. Coordination with M^{2+} metal ions usually occurs *via* the two S-atoms with loss of the ligand NH proton, and this leads to **2** and neutral bis(ligand)metal(II) complexes $[ML_2]$ with either a tetrahedral or square-planar geometry around the metal ion [19]. With Ru^{2+}, 5- and 6-coordinate structures of the types $[Ru(PPh_3)\{(S{=}PPh_2)_2N\}_2]$ and $[Ru(NH_3)(PPh_3)\{(S{=}PPh_2)_2N\}_2]$ have been reported [26], whilst, with Bi^{3+}, a neutral $[Bi\{(S{=}PPh_2)_2N\}_3]$ complex with a distorted octahedral geometry has been established [11]. Five-

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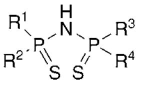
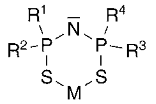
[1] For convenience, the general name 'dithioimidodiphosphato' is also used for $(S{=}PR_2)_2NH$ with R alkoxy or aryloxy.

coordinate trigonal bipyramidal structures with In^{3+} of the type $[InCl\{(S=Pr_2))_2N\}_2]$ ($R=Ph$, ${}^iPr$) are also known [22]. With Sm^{2+}, Y^{3+}, and other lanthanide ions, in addition to *S,S*-binding, terdentate coordination involving both S-atoms and the deprotonated N-atom has been found [25].



1 = HL^{a})



2 = $[ML]^{+}$ ^{a})

^{a}) For L, see *Table 1*.

When coordinated through the two S-atoms, 'dithioimidodiphosphato' ligands L[1]) are reminiscent of the well-known pentane-2,4-dionato chelators such as acetylacetonato ($acac^-$), but differ in forming nonplanar chelate rings with puckered P–N–P groups. The other significant difference is the presence of four bulky R groups attached to the P-atoms and flanking the donor S-atoms, compared with only two possible R groups attached to the carbonyl C-atoms of 1,3-diketones like pentane-2,4-dione (Hacac). The greater steric hindrance produced by the four bulky groups leads to the ready formation of neutral tetrahedral bis(ligand)metal(II) complexes with **1**, and such ligands have been developed for the selective hydrometallurgical extraction of some divalent metal ions. For example, a process for the selective removal of Zn^{2+} from Fe^{3+} (recovery of zinc from rusty galvanized steel) has been developed [31]. Theoretical calculations suggest that ligands containing an α-branched alkyl chain at the P-atom are good extractants for zinc(II), whereas those having a primary C-atom or an O-atom at the P-atom are poor extractants [20].

Early structural studies concentrated largely on the coordination chemistry of the tetraphenyl ligand $[Ph_2P(=S)]_2NH$ and to a lesser extent of the other symmetric tetraalkyl analogues $(S=PMe_2)_2NH$ and $(S=P^iPr_2)_2NH$ (${}^iPr$ = isopropyl), as well as of some unsymmetric ligands [1][2][6][9][10][12][13]. A comparison with other bidentate S_2-donors such as 1,1-dithiolato ligands shows that they have a smaller S$\cdots\cdots$S separation (*ca.* 3 Å) compared to $(SPNPS)^-$ ligands (*ca.* 4 Å), and this produces more strain in the tighter chelate ring. Whereas the 1,1-dithiolato ligands have been found to form square-planar bis(ligand)nickel(II) chelates, the analogous complexes with $[(S=PR_2)N(R_2P=S)]^-$ ligands are more frequently found to be tetrahedral (*e.g.*, R^1 to R^4 = Ph, Me, ${}^iPr$) [11][19][21][24]. This is believed to arise from the steric effects of the bulky R_2P groups which are in close proximity to the large S-donor atoms, although interestingly, the less-symmetric complex $[Ni\{(S=PPh_2)N(Me_2P=S\}_2]$ has been found to have a square-planar geometry [18].

In this study, we investigated 'dithioimidodiphosphato'[1]) ligands **1** (= HL) containing four bulky groups R^1 to R^4 that readily form neutral bis(ligand)metal(II) complexes with a range of transition and main-group metal ions M (*Eqn. 1*) in the presence of excess buffer base (B).

$$M^{2+} + 2HL + 2B(\text{base}) \rightleftharpoons [ML_2] + 2BH^+ \qquad (1)$$

For the ligands studied here (*Table 1*), all of the bis(ligand)metal(II) complexes have geometries close to tetrahedral at the metal center. X-Ray crystal structures of $[M(L^1)_2]$ and $[M(L^6)_2]$ have been determined for M = Co, Ni, Zn, and Hg, and found to have distorted tetrahedral geometries; square-planar geometries were established for the palladium(II) complexes $[PdL_2]$ ($L = L^5$ and L^6). These crystal structures will be reported elsewhere [24].

Table 1. *Structures of the Ligands* **1** ($= HL = [R^1R^2P(=S)]NH[P(=S)R^3R^4]$) *Investigated*

Ligand	R^1	R^2	R^3	R^4
HL^1	EtO	EtO	Ph	Ph
HL^2	cyclohexyl	cyclohexyl	cyclohexyl	cyclohexyl
HL^3	$Me(CH_2)_2CH(Me)$	$Me(CH_2)_2CH(Me)$	^iPr	^iPr
HL^4	$2,4\text{-}Me_2C_6H_3O$	$2,4\text{-}Me_2C_6H_3O$	Ph	Ph
HL^5	^iPrO	^iPrO	$2\text{-}^tBuC_6H_4O$	$2\text{-}^tBuC_6H_4O$
HL^6	^tBu	Bu	^tBu	Bu
HL^7	Me_2CHCH_2	Me_2CHCH_2	Me_2CHCH_2	Me_2CHCH_2
HL^8	^iPr	^iPr	^iPr	^iPr
HL^9	$2\text{-}^tBuC_6H_4O$	Ph	$2\text{-}^tBuC_6H_4O$	$2\text{-}(MeCH_2CH(Me))C_6H_4O$
HL^{10}	Ph	Ph	Ph	Ph
HL^{11}	PhO	PhO	PhO	PhO

Although there have been numerous synthetic and structural investigations of the complexes formed by such ligands, to date there have been no reports of the kinetics of formation and dissociation of such species. In this study, the stopped-flow technique was used to measure rates of formation and dissociation of complexes formed by Ni^{2+} and Co^{2+} ions, and to estimate some equilibrium formation constants (K) for the mono(ligand) complexes from the relationship $K = k_f/k_d$ where k_f and k_d are the rate constants for formation and dissociation of the metal/ligand 1:1 complexes, respectively.

Kinetic studies were also made of the reactions of Cu^{2+} with these ligands. Here the rates of formation of tetrahedral $[Cu(ligand)_2]$ were too fast to be measured at 25° with the available stopped-flow technique used ($t_{1/2} < 2$ ms), but subsequent slower redox reactions to give trinuclear Cu^+ complexes, $[Cu_3(ligand)_3]$, were measurable, and these rate constants are reported together with the UV/VIS spectrum of one of the rapidly formed tetrahedral $[Cu(ligand)_2]$ complexes. The X-ray structure of $[Cu_3(L^5)_3]$ was also determined and is in good agreement with that found for analogous copper(I) complexes [13][23]. A distorted tetrahedral Cu^I_4 cluster has recently been obtained from reactions of $[Cu(MeCN)_4]X$ ($X = BF_4$ or PF_6] with $(E = PPh_2)NH$ (E = S, Se) [30]. Crystal structures of $[M(Ph_3P)\{(S = PPh_2)_2N\}]$ ($M = Cu^I$, Ag^I, Au^I) are also reported [29].

Experimental. – *General.* The 'dithioimidodiphosphato' ligands **1** were obtained from *Zeneca Specialties*, with the exception of HL^7 which was prepared by reacting $^sBu_2P(=S)NH_2$ with $^sBu_2P(=S)Br$ as detailed below. Ligands HL^3 and HL^{11} were recrystallized from $CHCl_3$, and all other ligands from EtOH. All solvents and other reagents were obtained from *Aldrich*. Purity of the ligands was checked by NMR and MS measurements. Kinetic and spectroscopic measurements were made by using spectroscopic grade solvents. Metal solvates of formula $[M(solvent)_6][BF_4]_2$ (solvent = MeOH, DMSO) were prepared by a published method [32], and solns. were standardized by EDTA titration [33]. Kinetic measurements were made with an *Applied Photophyics-SX18-*

MV kinetic workstation, VIS and IR Spectra: *Philips Unicam-PU-87000* and *Perkin-Elmer Paragon-1000* spectrophotometers, resp.; in nm and cm^{-1}, resp. NMR Spectra: *Bruker ACP400* spectrometer; δ in ppm rel. to Me_4Si (^1H and ^{13}C) and H_3PO_4 (^{31}P), J in Hz. Mass spectra: *Kratos MS80* instrument; in *m/z*. Elemental analyses: (C,H,N): *Leeman-Labs CE440* instrument.

Bis(2-methylpropyl)phosphinothioic Bromide ($^{s}Bu_2P(=S)Br$). Under anh. conditions, a soln. of $P(=S)Cl_3$ (101.6 g, 0.60 mol) in dry Et_2O (200 ml) was added dropwise with overhead stirring to an ice-cold soln. of $^{s}BuMgCl$ (210.4 g, 1.8 mol) in Et_2O (200 ml). After the addition, the mixture was allowed to warm to r.t. and then heated under reflux for 2 h. After cooling, the mixture was quenched with aq. 2M HCl (1 l). The aq. layer extracted with more Et_2O (3 × 200 ml) and the combined Et_2O extract dried ($MgSO_4$), and evaporated to leave a pungent oily residue ($^{s}Bu_4P_2S_4$). The oil was dissolved in CH_2Cl_2 (400 ml), the soln. cooled to 0°, and a soln. of Br_2 (57.5 g, 0.36 mol) in CH_2Cl_2 (400 ml) added dropwise with stirring to give a pink-brown soln. After warming to r.t., the solvent was evaporated and the orange liquid product distilled at 120–122°/2.5 Torr): $^{s}Bu_2P(=S)Br$. $^{31}P\{^1H\}$-NMR: 120.5 (*s*).

P,P-*Bis(2-methylpropyl)phosphinothioic Amide* ($^{s}Bu_2P(=S)NH_2$). NH_3 Gas was bubbled through a soln. of $^{s}Bu_2P(=S)Br$ (9 g, 0.045 mol) in THF (100 ml) for 1 h. Distilled H_2O was added to dissolve any NH_4Br and excess NH_3. The aq. layer was extracted with more THF (3 × 100 ml) and the combined THF extract dried ($MgSO_4$) and evaporated: $^{s}Bu_2P(=S)NH_2$. Colorless oil. $^{31}P\{^1H\}$-NMR: 79.63 (*t*).

P,P-*Bis(2-methylpropyl)*-N-*[bis(2-methylpropyl)phosphinothioyl]phosphinothioic Amide* ($HL^7 = (S{=}P^{s}Bu_2)_2NH$). To an ice-cold slurry of NaH (4.5 g of a 60% dispersion in paraffin oil) in THF (200 ml), a soln. of $^{s}Bu_2P(=S)NH_2$ (8 g, 58.8 mmol) in THF (30 ml) was added under stirring at 0°. The mixture was allowed to warm to r.t., then left for 30 min before cooling again to 0°. A soln. of $^{s}Bu_2P(=S)Br$ (9 g, 0.045 mol) in THF (30 ml) was added dropwise with stirring, and the mixture was then heated overnight under reflux. After cooling, distilled H_2O (50 ml) was added cautiously to destroy any excess NaH. Conc. HCl soln. was then added dropwise until the mixture was acidic. The solvent was evaporated and the residue extracted with Et_2O (50 ml). The Et_2O extract was washed with H_2O (3 × 30 ml), dried ($MgSO_4$), and evaporated and the oily residue taken up in dry hexane (5 ml) and left at 0° to produce white crystals of HL^7 (3.73 g). IR: 3215 (ν(NH)); 900, 959, 767 ν(PNP)); 1296 (δ(NH)). ^1H-NMR ($CDCl_3$): 1.02 (*t*, ^3J(H,H) = 7.33, 12 H); 1.25 (*m*, ^2J(P,H) = 7.32, 7.32, ^3J(H,H) = 1.36, 12 H); 1.39 (*m*, 4 H); 1.97 (*m*, 4 H); 2.25 (*m*, 4 H); 2.81 (*t*, ^2J(P,H) = 7.34, 1 H). ^{13}C-NMR ($CDCl_3$): 12.45 (*m*, 4 C); 13.34 (*s*, 4 C); 23.47 (*m*, 4 C); 39.93 (*m*, 4 C). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 89.70 (*m*, ^2J(P,H) = 12.39, ^2J(P,P) = 19.28). FAB-MS (pos.): 370 (M^+).

*Tris{*P,P-*bis[2-(1,1-dimethylethyl)phenyl]*-P′,P′-*bis(1-methylethyl)dithioimidodiphosphato}tricopper(I)* ($[Cu^I_3(L^5)_3]$). A soln. of $[Cu(H_2O)_6][BF_4]_2$ (21 mg, 0.0896 mmol) in EtOH (5 ml) was added to a soln. of HL^5 (0.10 g, 0.179 mmol) in EtOH (5 ml) to give a deep purple soln. This deep purple soln. slowly decolorized to give a pale pink soln. from which X-ray-quality crystals precipitated after a few hours and were collected by filtration. Yield 88 %. $^{31}P\{^1H\}$-NMR ($CDCl_3$): 37.2 (*d*); 33.8 (*d*); (^2J(P,P) 45.8. FAB-MS (pos.): 1867 ($[Cu_3(L^5)_3]^+$). Anal. calc. for $C_{26}H_{41}CuNO_4P_2S_2$: C 50.3, H 6.65, N 2.25; found: C 50.3, H 6.68, N 2.43.

The X-ray structure of $[Cu^I_3(L^5)_3]$ is shown in *Fig. 1*, and selected bond lengths and angles are collected in *Table 2*.

X-Ray Crystallography: Data Collection and Processing. The crystal of $[Cu^I_3(L^5)_3]$ was held at 180(2) K with an *Oxford-Cryosystem-Cryostream* cooler. Data were collected with a *Siemens Smart-CCD*-area-detector diffractometer. A full hemisphere of reciprocal space was scanned by a combination of three sets of exposures; each set had a different φ angle for the crystal, and each exposure of 10 s covered 0.3° in ω. The crystal-to-detector distance was 5.01 cm. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflection; a multi-scan absorption correction was applied by using SADABS [34]. The structures were solved by direct methods with SHELXTL-PC [35] and refined by full matrix least-squares on F^2 for all data with SHELXL-97 [36]. H-atoms were added at calculated positions and refined using a riding model. Anisotropic temperature factors were used for all non-H-atoms; H-atoms were given isotropic temperature factors equal to 1.2 (or 1.5 for Me H-atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC-254186²).

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2) Copies of the data can be obtained free of charge on application to *CCDC*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

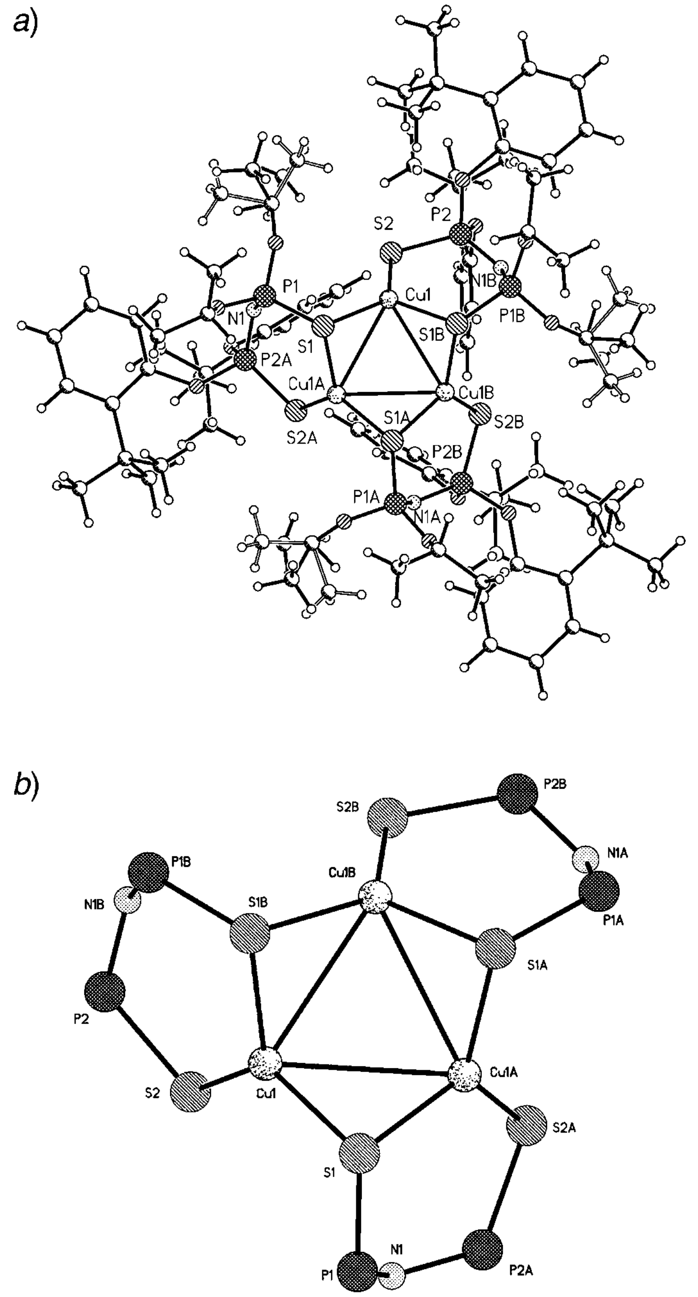


Fig. 1. a) *Structure of* $[Cu^I_3(L^5)_3]$ *showing the atomic numbering* (H-atoms omitted for clarity). b) *Structure of* $[Cu^I_3(L^5)_3]$ *showing the atomic numbering* (H-, O-, and C-atoms omitted)

Table 2. *Selected Bond Lengths and Angles in* $[Cu^{I}_{3}(L^{5})_{3}]$[a]). Arbitrary numbering.

	Bond lengths [Å]		Bond angle [°]
Cu(1)–S(2)	2.216(2)	S(2)–Cu(1)–S(1)	128.92(8)
Cu(1)–S(1)	2.264(2)	S(2)–Cu(1)–S(1)#1	122.81(8)
Cu(1)–S(1)#1	2.272(2)	S(1)–Cu(1)–S(1)#1	108.16(11)
Cu(1)–Cu(1)#1	2.9785(16)	S(2)–Cu(1)–Cu(1)#1	115.98(6)
Cu(1)–Cu(1)#2	2.9785(16)	S(1)–Cu(1)–Cu(1)#1	98.91(6)
S(1)–P(1)	2.018(3)	S(1)#1–Cu(1)–Cu(1)#1	48.83(6)
S(1)–Cu(1)#2	2.272(2)	S(2)–Cu(1)–Cu(1)#2	119.46(5)
S(2)–P(2)	1.975(2)	S(1)–Cu(1)–Cu(1)#2	49.08(6)
P(1)–O(11)	1.505(8)	S(1)#1–Cu(1)–Cu(1)#2	98.71(6)
P(1)–N(1)	1.549(6)	Cu(1)#1–Cu(1)–Cu(1)#2	60.0
P(1)–O(12)	1.553(6)	P(1)–S(1)–Cu(1)	105.30(10)
P(2)–O(22)	1.578(4)	P(1)–S(1)–Cu(1)#2	102.44(10)
P(2)–N(1)#1	1.582(6)	Cu(1)–S(1)–Cu(1)#2	82.09(7)
P(2)–O(21)	1.593(4)	P(2)–S(2)–Cu(1)	103.71(9)

[a] #1 means A; #2 means B.

Results. – *Studies of the Formation of Nickel(II) and Cobalt(II) Complexes.* To drive the equilibrium of *Eqn. 1* to the right, an excess of ligand (HL) and an excess of buffer base (B) was used. Studies were made either in 100% MeOH in the presence of 2,6-dimethylpyridine (2,6-lutidine) as buffer, or in MeOH/H_2O 95:5 (*v*/*v*; for solubility reasons) in the presence of 3-(morpholin-4-yl)propane-1-sulfonic acid (MOPS) as buffer. These two buffers were chosen since they do not form complexes with the metal ions, and because they have pK_a values around 6–7 where the 'dithioimidodiphosphates' are not deprotonated before coordination to the metal ions. *Job*'s method of continuous variations [37] confirmed the formation of a ligand/metal 2:1 complex, and the molar extinction coefficients of both the mono- and bis(ligand)nickel(II) complexes ($\varepsilon > 150$ l mol^{-1} cm^{-1}) were consistent with the formation of tetrahedral rather than octahedral complexes. Typical spectra of the d–d bands obtained in MeOH for the ligand/nickel(II) 1:1 and 2:1 complexes recorded for ligand HL^3 in the presence of either excess Ni^{2+} or excess HL^3, respectively, are shown in *Fig. 2*. The spectra are as expected if both the mono- and bis-ligand species have a tetrahedral geometry, based on the relatively large molar extinction coefficients compared with those for octahedral complexes that normally have ε values for the d–d bands in the range of 10–20 l mol^{-1} cm^{-1} [38]. The d–d bands are at longer wavelength for $[Ni(L^3)(MeOH)_2]^+$ compared with $[Ni(L^3)_2]$ as expected for the greater ligand-field strength of the latter.

For reactions with Ni^{2+}, initial kinetic studies were investigated in MeOH solution in the presence of 2,6-lutidine buffer. Stopped-flow experiments were carried out by using excess ligand ($5 \cdot 10^{-4}$ M) over $[Ni^{2+}]$ ($5 \cdot 10^{-5}$ M), and with [2,6-lutidine] (0.020M) in large excess. The ionic strength was controlled by addition of $[Bu_4N][BF_4]$ (0.010M). Reactions were monitored at 25.0° and 380 nm and revealed a single exponential kinetic trace. The observed pseudo-first-order rate constants were interpreted as that associated with the formation of the tetrahedral mono(ligand)nickel(II) complexes, $[NiL(MeOH)_2]^+$, with rapid conversion of $[NiL(MeOH)_2]^+$ to $[NiL_2]$ (*Eqns. 2* and *3)*.

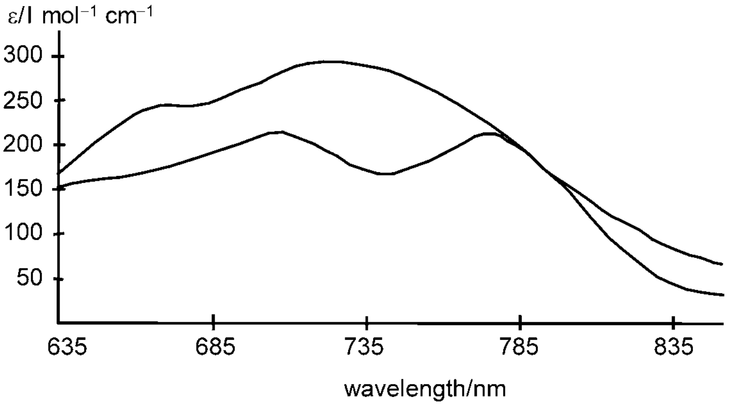


Fig. 2. *VIS Spectra for the d–d bands of tetrahedral* $[Ni(L^3)(MeOH)_2]^+$ (lower trace) *and* $[Ni(L^3)_2]$ (upper trace) *in MeOH containing 2,6-lutidine buffer* (0.1M). Upper trace: $[HL^3] = 5 \cdot 10^{-3}$ M and $[[Ni(MeOH)_6][BF_4]_2] = 5 \cdot 10^{-5}$ M; lower trace: $[HL^3] = 5 \cdot 10^{-4}$ M and $[[Ni(MeOH)_6][BF_4]_2] = 5 \cdot 10^{-2}$ M, with allowance made for the absorbance of excess Ni^{2+}

$$[Ni(MeOH)_6]^{2+} + HL + B\ (buffer) \rightarrow [NiL(MeOH)_2]^+ + 4\ MeOH + BH^+ \tag{2}$$

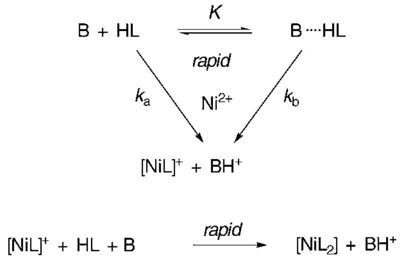
$$[NiL(MeOH)_2]^+ + HL + B \rightarrow [NiL_2] + 2\ MeOH + BH^+\ (\textit{rapid}) \tag{3}$$

The pseudo-first-order rate constants (k_{obs}) were found to increase with the concentration of the 2,6-lutidine buffer [B] as shown in *Fig. 3* for the reactions with ligand HL^3. The data plotted in *Fig. 3* were fitted to *Eqn. 4* by using nonlinear least-squares analysis to give the continuous curve shown in *Fig. 3*.

$$k_{obs} = \frac{a + b[B]}{1 + K[B]} \tag{4}$$

K is the equilibrium constant for the rapid H-bonding of HL with B ($K = [B \cdots HL]/[B][HL]$), and a and b are constants. *Scheme 1* fits the observed variation of k_{obs} with [B].

Scheme 1



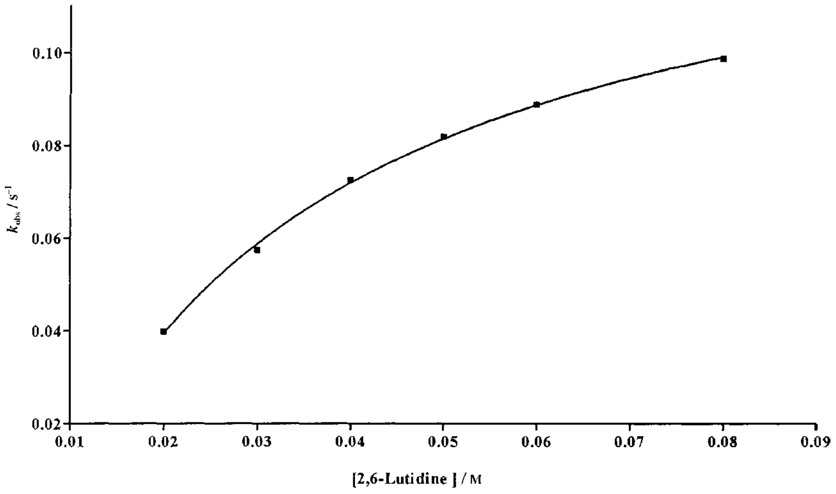


Fig. 3. *Plot of the pseudo-first-order rate constants* (k_{obs}) vs. *2,6-lutidine buffer concentration at 25° for the reaction of* Ni^{2+} ($5 \cdot 10^{-5}$ M) *with* HL^3 (10^{-3} M) *at ionic strength controlled by* $[Bu_4N][BF_4]$ (0.1M). The continuous curve was calculated by using a nonlinear least-squares fit to *Eqn. 4*

k_a and k_b are the rate constants for reactions of Ni^{2+} with non-H-bonded and H-bonded buffer–ligand species, respectively. These two reactions, that each involve formation of $[Ni(L)]^+$, are the rate-determining steps for the overall reactions to give $[Ni(L)_2]$. The rate law associated with *Scheme 1* is outlined in *Scheme* 2.

Scheme 2

$$\frac{d[NiL_2]}{dt} = k_a[Ni^{2+}][HL] + k_b[Ni^{2+}][B\cdots HL] = -\frac{1}{2}\frac{d}{dt}([HL] + [B\cdots HL])$$

hence,

$$[Ni^{2+}][HL]\{k_a + k_bK[B]\} = -\frac{1}{2}\frac{d}{dt}[HL]\ (1 + K[B])$$

and in the presence of excess HL and B,

$$-\frac{d[HL]}{dt} = \frac{2[Ni^{2+}][HL](k_a + k_bK[B])}{1 + K[B]} = k_{obs}[Ni^{2+}]$$

where,

$$k_{obs} = \frac{2[HL](k_a + k_bK[B])}{1 + K[B]}$$

in agreement with the observed *Eqn. 4* where

$$a = 2k_a[HL],\ b = 2k_bK[HL] \text{ and } b/a = k_bK/k_a$$

With 2,6-lutidine as buffer, it is possible to determine an approximate equilibrium constant for the buffer–ligand interaction in MeOH (for L^3, $K = (42.5 \pm 8.5)$ l mol^{-1}], but the rate constants determined this way were too inaccurate. Therefore, an alternative buffer 3-(morpholin-4-yl)propane-1-sulfonic acid (MOPS) was selected to allow a more-accurate estimation of the formation rate constants. MOPS has poorer H-bonding properties compared with 2,6-lutidine, and at the concentration used does not affect the observed rate constants.

Kinetic Studies of the Complex Formations in the Presence of the Buffer MOPS. MOPS has a pK_a of 7.2 in H_2O but is not soluble enough in MeOH; thus investigations were carried out in MeOH/H_2O 95 : 5 (*v*/*v*). Spectrophotometric titrations showed that the equilibrium of *Eqn. 1* is driven to the right in the presence of excess [MOPS] (0.02M). Kinetic studies were carried out at 25.0° under pseudo-first-order conditions by using the stopped-flow method with [ligand] in large excess ($(1-15)\cdot 10^{-3}$ M) over [metal ion] ($5\cdot 10^{-5}$ M). Ligand solutions were freshly prepared prior to each set of measurements to avoid any possible ligand decomposition. Equimolar amounts of MOPS were added to the metal ion and the ligand solutions before mixing, and rate data were collected at 380 nm. A single pseudo-first-order rate process was observed, and plots of the observed pseudo-first order rate constants, k_{obs}/s^{-1} *vs.* [ligand] were linear with k_{obs} close to zero at zero [ligand]. A typical plot for the reaction of Ni^{2+} with HL^3 is shown in *Fig. 4*, and from such plots, the second-order rate constants for complex formation were obtained from the slopes of the lines by using weighted linear least-squares analysis (*Table 3*). For these calculations, the observed rate constants (k_{obs}) were weighted by the inverse square of their standard deviations. Values of k_{obs} were the average of at least 3 measurements at each ligand concentration. Studies of the rates of the formation reactions with ligands HL^3, HL^6, HL^7, HL^8 (all carrying aliphatic substituents) were all possible in MeOH/H_2O 95 : 5 by the stopped-flow method, but studies of all of the ligands substituted with alkoxy, aryl, and aryloxy groups were outside the range of this technique. For the latter, this is attributed to the smaller

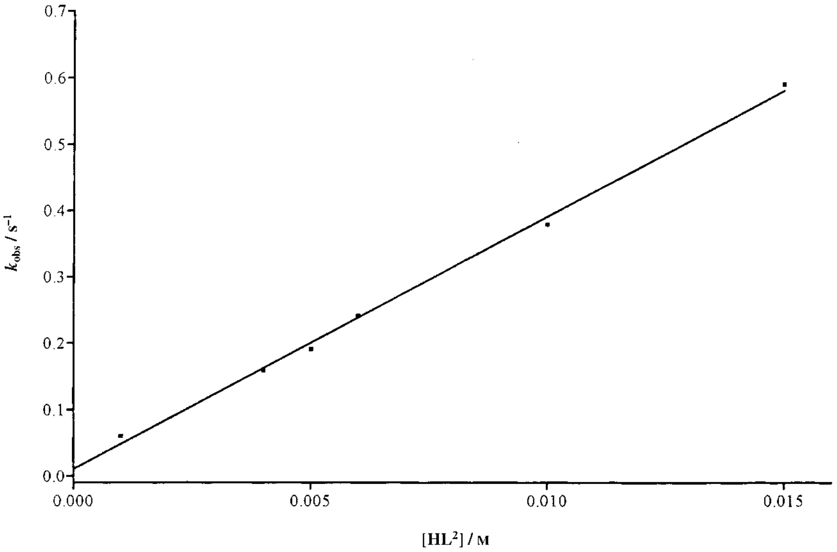


Fig. 4. *Plot of the pseudo-first-order rate constants* (k_{obs}) *at 25°* vs. *[HL^3] for the reaction with Ni^{2+}* ($5\cdot 10^{-5}$ M) *in MeOH/H_2O 95 : 5* (*v*/*v*) *containing MOPS buffer* ($2\cdot 10^{-2}$ M)

Table 3. *Comparison of Rate Constants at 25.0° for the Formation* (k_f) *and Dissociation* (k_d) *of Tetrahedral Mono(ligand)metal(II) Complexes of* Ni^{2+} *and* Co^{2+} *with Four 'Dithioimidodiphosphate' Ligands in MeOH/*H_2O *95:5* (*v*/*v*), *and the Kinetically Determined Equilibrium Formation Constants,* $K = k_f/k_d$

Ligand	Ni^{2+}			Co^{2+}		
	k_f [l mol^{-1} s^{-1}]	10^4 k_d [s^{-1}]	$10^{-5}K$ [l mol^{-1}]	k_f [l mol^{-1} s^{-1}]	10^4 k_d [s^{-1}]	$10^{-5}K$ [l mol^{-1}]
HL^3	38.1 ± 1.0	7.55 ± 0.01	0.50 ± 0.01	731 ± 33	44.67 ± 0.01	1.64 ± 0.07
HL^6	119.4 ± 2.7	6.34 ± 0.05	1.88 ± 0.04	3113 ± 41		
HL^7	55.3 ± 0.6	4.35 ± 0.06	1.27 ± 0.02	1023 ± 37	12.90 ± 0.01	7.93 ± 0.09
HL^8	43.5 ± 2.0	4.92 ± 0.02	0.88 ± 0.04	867 ± 29	22.55 ± 0.09	3.84 ± 0.13

equilibrium formation constants, resulting in large rate constants for the back (dissociation) reactions.

The ligands HL^2, HL^{10}, and HL^{11} are too insoluble for studies in MeOH/H_2O, so studies were attempted in $CHCl_3$/DMSO 95:5 (*v*/*v*). The DMSO was used to allow sufficient solubility of the $[Ni(DMSO)_6][BF_4]_2$ salt used. The buffer MOPS does not dissolve in this solvent mixture, so the sterically hindered base 1,4-diazabicyclo[2.2.2]octane (DABCO) was chosen instead. For HL^2, the reaction rates in $CHCl_3$/DMSO were measured at 25° in the presence of excess ligand ($2.5 - 12.5 \cdot 10^{-4}$ M) over $[Ni^{2+}]$ ($5 \cdot 10^{-5}$ M) in the presence of DABCO ($3 \cdot 10^{-3}$ M) buffer and $[Bu_4N][BF_4]$ (10^{-2} M) for ionic strength control. For HL^2 that carries cyclohexyl substituents, the second-order rate constant in $CHCl_3$/DMSO 95:5 (*v*/*v*) was found to be 4391 ± 265 l mol^{-1} s^{-1} at 25°. This was obtained from the slope of the plot of k_{obs} *vs.* $[HL^3]$. Attempts to study HL^{10} and HL^{11} that carry aromatic substituents were again unsuccessful due to too rapid conversions for measurements by the available stopped-flow method.

Reactions of $[Co(MeOH)_6][BF_4]_2$ with ligands HL^3, HL^6, HL^7, and HL^8 were studied in MeOH/H_2O 95:5 (*v*/*v*) at 365 nm under the same conditions as those used for the nickel(II) measurements. As expected, the reactions were more rapid than for nickel(II), in line with the greater solvent-exchange rate for cobalt(II). The rate constants are collected in *Table 3*.

Kinetic Studies of the Complex Dissociation Reactions. Reversal of the equilibrium of *Eqn. 1* is possible by addition of an excess of 2,6-lutidinium tetrafluoroborate. Solutions of largely the mono(ligand)metal(II) complexes were prepared by mixing excess M^{2+} ion (0.020M; M = Ni or Co) with ligand (10^{-3} M) in MeOH/H_2O 95:5 (*v*/*v*) containing 2,6-lutidine (10^{-2} M) and $[Bu_4N][BF_4]$ (0.1M). A second series of solutions of 2,6-lutidinium tetrafluoroborate (0.01 – 0.10M) were prepared in the same solvent mixture, and the ionic strength was maintained at 0.10 by addition of the requisite amount of $[Bu_4N][BF_4]$. The dissociation reactions were monitored by mixing the complex and 2,6-lutidinium solutions at 25° and following the absorbance decreases at either 380 or 365 nm for the nickel(II) and cobalt(II) complexes, respectively. A single first-order reaction was observed in each case, and the observed rate constants were found to increase only slightly as the concentration of the 2,6-lutidinium ion was increased. The dissociation rate constants in *Table 3* were obtained from plots of k_{obs} *vs.* [2,6-lutidinium ion] extrapolated to [2,6-lutidinium ion] = 0.

Kinetic, Equilibrium, and Structural Studies of the Reactions of 'Dithioimidodiphosphates' with Cu^{2+} *Ion.* Previous studies of the reactions of 'dithioimidodiphosphates' with copper(II) have been shown to involve rapid formation of intensely colored bis(ligand)copper(II) complexes followed by reduction of these intermediates to colorless copper(I) complexes of varying stoichiometry. In the presence of triphenylphosphine, a mononuclear complex $[Cu(Ph_3P)\{(S=PPh_2)_2N\}]$ was isolated and characterized by means of an X-ray crystal structure [15]. An early attempt to prepare a copper(II) complex led to the isolation of a copper(I) product [3], but a later study involving the reaction of $K[(S=PPh_2)_2N]$ with $CuCl_2$ at – 78° led to the isolation of the dark blue copper(II) complex $[Cu\{(S=PPh_2)_2N\}_2]$. At 25° in CH_2Cl_2 solution, this blue product was reported to be reduced to a Cu^I product with a first-order rate constant of *ca.* $2 \cdot 10^{-3}$ min^{-1} [7]. In further studies of this reaction, the Cu^I product was isolated and characterized by a crystal structure as $[Cu_4L_3][CuCl_2] \cdot CCl_4$ ($HL = (S=PPh_2)_2NH$) that dissociated to $[Cu^I_3L_3]$ plus the oxygenated ligand $(HOPPh_2)N(PPh_2=S)$ and elemental sulfur [8]. Involvement of moisture in these reactions was indicated by our study of analogous reactions of Cu^{2+} with HL^5 in EtOH and MeCN. At room temperature, $[Cu(H_2O)_6][BF_4]_2$ and 2 mol-equiv. of HL^5 in EtOH immediately formed a deep purple solution which was reduced to a Cu^+ product that precipitated as white $[Cu^I_3(L^5)_3]$. This was characterized by ^1H-, ^{13}C-, and ^{31}P-NMR, an elemental analysis, a FAB mass spectrum, and an X-ray crystal structure (*Fig. 1*). When $[Cu(MeCN)_6][BF_4]_2$ was treated with HL^5 under dry Ar in dry MeCN, with either a $Cu(II)/HL^5$ 1:1 or 1:2 stoichiometry, the purple solution was again obtained which persisted for several hours. However, upon exposure of this purple solution to moisture from the air, a solid precipitate of $[Cu^I_3(L^5)_3]$ was obtained which was examined by ^{31}P-NMR. Besides the complex, it contained mainly free ligand; but also a new resonance appeared at δ 1.31, in line with some formation of the oxygenated ligand $[(Me_2CHO)_2P=O]NH[(2\text{-}^tBuC_6H_4O)_2P=S]$ (HL'). A yellow residue of sulfur was also found. By comparison of these observations with those of related studies [8], the overall reaction of *Eqn. 5* was deduced to have occurred.

$$6\,Cu^{2+} + 9\,HL^5 + 3\,H_2O \rightarrow 2[Cu_3(L^5)_3] + 3\,S + 3\,HL' + 12\,H^+ \qquad (5)$$

Stopped-flow kinetic studies were carried out with unbuffered solutions. When HL^3 ($5 \cdot 10^{-4}$ M) was reacted with $[Cu(MeOH)_6][BF_4]_2$ ($5 \cdot 10^{-5}$ M) [26] at 25° in MeOH, the last stages of the very rapid formation of highly colored $[Cu(L^3)_2]$ was just detected at 380 nm. This reaction was followed by a much slower fall in absorbance as the reduction to colorless $[Cu_3(L^3)_3]$ occurs. The rate constant for the formation of the bis(ligand)-copper(II) intermediate could not be measured reliably, but the spectrum of $[Cu(L^3)_2]$ was obtained 2 ms after mixing by means of a variable-wavelength stopped-flow experiment, conducted over the wavelength range 320–650 nm (*Fig. 5*).

Two intense absorption bands were found at λ_{max} (ε/l mol^{-1} cm^{-1}) 580 (4990) and 390 (4480) nm. These two bands are similar to those recorded for the tetrahedral $[Cu\{(S=PPh_2)_2N\}_2]$ in CH_2Cl_2, *i.e.*, λ_{max} at 575 (3610) and 407 (4100) nm. This latter complex was isolated at – 78°, and an approximate spectrum obtained immediately after dissolving in CH_2Cl_2 [7]. Further stopped-flow studies of the reactions of $[Cu(MeOH)_6]^{2+}$ ($5 \cdot 10^{-5}$ M) with variable amounts of HL^3 (5 to $20 \cdot 10^{-5}$ M) showed that the maximum absorbance for $[Cu(L^3)_2]$, recorded by the stopped-flow technique 2 ms after mixing,

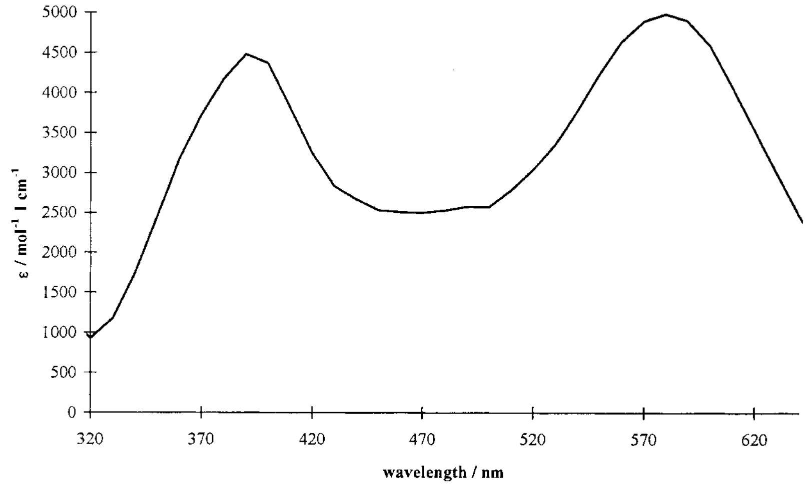


Fig. 5. *UV/VIS Spectrum of [Cu(L^3)$_2$] Recorded between 340 and 650 nm by means of a stopped-flow multiwavelength experiment, with absorbances measured 2 ms after reacting [Cu(MeOH)$_6$][BF$_4$]* ($5 \cdot 10^{-5}$ M) *with excess HL^3* ($5 \cdot 10^{-4}$ M) *in MeOH at 25°*

occurred when the metal/ligand ratio was 1:2, thus confirming the formation of the bis(ligand)copper(II) species.

The rate constants for the reduction of [CuL_2] species to give [$Cu^{x}{}_3L_3$] ($L = L^{11}$, L^1, L^4, L^5, L^9, L^3, L^8, and L^7 in order of decreasing rate) were measured keeping ligand/copper(II) $\geq 10:1$. A single first-order rate process was observed in each case, and the rate constants at 25° are collected in *Table 4.* The rates did not vary as the excess ligand concentration was increased by a factor of four.

Table 4. *Rate Constants at 25° for the Formation of [$Cu^I{}_3L_3$] from [$Cu^{II}L_2$]*. Standard deviations in parentheses.

L	L^{11}	L^1	L^4	L^5	L^9	L^3	L^8	L^7
10^5 k/s^{-1}	2849(7)	1110(4)	154(4)	21.0(0.1)	12.9(0.1)	5.00(0.03)	4.52(0.04)	2.58(0.03)

Discussion. – Of the 'dithioimidodiphosphate' ligands investigated (*Table 1*), only those with electron-donating alkyl substituents, as opposed to the electron-withdrawing alkoxy, aryl, or aryloxy substituents, on the P-atom react slowly enough for measurements of rates of formation and dissociation of their metal complexes with Ni^{2+} and Co^{2+} ions by means of the available stopped-flow technique ($t_{1/2} > 2$ ms). Reactions of Ni^{2+} and Co^{2+} ions with HL^3, HL^6, HL^7, and HL^8 were measured and found to involve formation of tetrahedral [ML(solvent)$_2$]$^+$ ions (M = Co, Ni) in the rate-determining step, followed by rapid conversion of [ML(solvent)$_2$]$^+$ to the tetrahedral [ML_2] products. This behavior is understandable since rates of solvent exchange usually control the rates of complex formation (the *Eigen–Wilkins* mechanism [39]), and solvent exchange with octahedral [M(solvent)$_6$]$^{2+}$ ions are much slower than with tetrahedral [ML(solvent)$_2$]$^+$ ions [39]. The tetrahedral geometries of [ML(solvent)$_2$]$^+$

and [ML_2] complexes was established from their VIS spectra (*e.g.*, *Fig. 2*), and from X-ray structures of some of the [ML_2] complexes [24].

From the data in *Table 3*, it can be seen that the rates of complex formation for Ni^{2+} are more than an order of magnitude slower than for Co^{2+}, which is in line with the relative rates of solvent exchange for the [$M(solvent)_6$]$^{2+}$ ions [40]. Rates of dissociation of the [$NiL(solvent)_2$]$^+$ ions are also slower than those of corresponding [$CoL(solvent)_2$]$^+$ ions, by factors of *ca.* 3–6. However, the smaller variation in values of the dissociation rate constants, $k_d(Ni^{2+})/k_d(Co^{2+})$, compared with the greater variation in values of the formation rate constants, $k_f(Ni^{2+})/k_f(Co^{2+})$, results in stability constants ($K = k_f/k_d$) for the Co^{2+} complexes being larger than those of Ni^{2+}. For octahedral metal complexes, stability constants usually vary according to the *Irving–Williams* sequence $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, which is in line with calculated variations in ligand-field stabilization energies (LFSE), with allowance being made for the greater LFSE for Cu^{2+} due to *Jahn–Teller* distortion. For the tetrahedral complexes of the M^{2+} ions studied here, the trend $K_{Ni} < K_{Co}$ contrasts with that found for octahedral complexes where $K_{Ni} > K_{Co}$, but is consistent with calculations of LFSE for tetrahedral systems. The $e^4t_2^3$ electronic configuration of Co^{2+} ions in a tetrahedral ligand field results in greater stability than for Ni^{2+} due to a calculated LFSE of $(-6/5)\Delta_t + 2P$ for Co^{2+} (P = pairing energy Δ_t = tetrahedral-ligand-field splitting parameter), compared with the $e^4t_2^4$ configuration of Ni^{2+} that gives a smaller calculated LFSE of $(-4/5)\Delta_t + 3P$. Therefore, ligands that force a tetrahedral geometry on first-row d-block M^{2+} ions are expected to be the most stable for Co^{2+}, in line with the results in *Table 3*.

The hydrometallurgical use of 'dithioimidodiphosphates' to extract divalent metal ions is aided by the formation of neutral [ML_2] complexes that extract from aqueous media into organic solvents like kerosene, but a complication arises due to the redox reactions observed with Cu^{2+} ions. Although formation of [CuL_2] species is very rapid, reduction to Cu^+ species follows to give multinuclear products such as [Cu_4L_3]$^+$ [8] and [Cu_3L_3] (*Fig. 1*) [17] and destruction of some of the extractant ligand. Therefore, effective use of such ligands in hydrometallurgy requires the careful removal of oxidizing metal ions like Cu^{2+} beforehand. The rates of the reduction reactions to give [Cu_3L_3] (*Table 4*) vary by at least a factor of 10^3, with those ligands carrying elcctron-withdrawing substituents like L^1 and L^{11} being much more reactive than those with electron-donating substituents like L^3, L^7, and L^8.

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