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Phenanthroline complexes of the d^{10} metals nickel(0), zinc(II) and silver(I)—comparison to copper(I) species

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Abstract—Structural features and physical properties of dmphen (2,9-dimethyl-1,10-phenanthroline) complexes with d^{10} metals Zn^{II}, Ni^0 and Ag^I were determined. These, together with the more well-known Cu^I compounds, constitute a rare example of an Ni^0, Cu^I, Zn^{II} isoelectronic, isostructural series. The first homoleptic zinc dmphen compounds $[ZnNO_3(dmphen)_2]NO_3$ (**1**) and $Zn(dmphen)_2(BF_4)_2$ (**2**) were prepared. Their structures were determined by X-ray crystallography. Compound **1** is five-coordinate, with one nitrate ion coordinated. Compound **2**, of the same stoichiometry as **1**, exhibits the pseudotetrahedral, four-coordinate $Zn(dmphen)_2^{2+}$ cation, which is isoelectronic and isostructural with the more well known $Cu(dmphen)_2^+$ cation. $Ni(dmphen)_2$ (**4**) was prepared for the first time. Reaction of $Ni^0(cyclooctadiene)_2$ with dmphen in ethanol or tetrahydrofuran gave crystals of dark blue $Ni^0(dmphen)_2$ (**4**). NMR experiments show that **4** is diamagnetic, with chemically equivalent dmphen ligands. From this species, by reaction with dichloromethane, $Ni_2(dmphen)_2Cl_4$ (**5**) was obtained. In this compound each nickel atom bears one terminal chloride ligand and the two nickel atoms are connected by two μ-chlorine atoms. Finally, $Ag(dmphen)_2BF_4$ (**6**) was prepared, which now extends the isostructural series described above to a second-row transition metal. The structure of this compound was determined by X-ray crystallography. © 1997 Elsevier Science Ltd

Keywords: phenanthroline; antiviral; d^{10}; fusion; membrane; pseudotetrahedral; tetrahedral-enforcer; copper; zinc; silver; nickel.

In a search for biologically active transition metal compounds, we have discovered [1] a variety of copper(I) phenanthroline complexes. In this previous work, we clearly demonstrated that, barring steric constraints, pseudotetrahedral complexes with $Cu(dmphen)_2^+$ (dmphen: 2,9-dimethyl-1,10-phenanthroline) stoichiometry form in preference to those of equimolar composition. It has been shown [2] that one such copper(I) complex (using a phenanthroline ligand bearing sulfonate groups) inhibits the HIV-1 protease *in vitro*. This complex has also been shown to inhibit replication of HIV [3]. The mechanism of antiviral activity for anionic compounds of this kind is believed [4] to involve inhibition of viral membrane fusion. The process of membrane fusion/viral entry is attracting increased attention with the recent discovery [5] of cellular cofactors which appear to mediate these events. The construction of pharmacologically active molecules about a copper(I) template dictates the use of phenanthrolines substituted in the 2 and 9 positions, which one might term [6] "tetrahedral enforcers". These ligands greatly enhance the stability of the +1 oxidation state of copper [7]. Furthermore, it has been found [8] that complexe of phenanthrolines lacking substitution at positions 2 and 9 can be mutagenic (by DNA intercalation), while those substituted in these positions generally are not. For these reasons, we became interested in other d^{10} complexes with dmphen derivatives as sources of useful biological activity and as a means to better understand the behavior of this class of compounds.

Although phenanthroline complexes of many metals are known, we were somewhat surprised by the absence of other homoleptic d^{10} $M(dmphen)_2$ species

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[Ni(bipyridyl)$_2$ has been prepared by metal atom vapor synthesis [9]]. For this reason, we sought to extend this body of knowledge to include some other metals and show that the M(dmphen)$_2$ pseudotetrahedral structure is general for d^{10} metals. In the present work we have demonstrated the first preparations of d^{10} bis-dmphen species from nickel(0), zinc (II) and silver(I). These species exhibit some properties which can be explained on the basis of periodic trends and by analogy to copper(I) compounds. In addition, we have added some thermodynamic characterization of the zinc species which, in combination with similar recently disclosed [7] studies of the copper(I) compounds, gives a consistent picture of the chemistry of these metal phenanthrolines.

RESULTS AND DISCUSSION

When a solution of dmphen is mixed with 1/2 equiv. of a source of zinc(II), nickel(0) or silver(I) crystalline products are obtained. In the case of nickel(0), the product possesses intense color, apparently due to a charge-transfer absorbance. With the zinc and silver dmphen complexes, the charge-transfer band appears to occur at higher energy than in the analogous copper compounds and the corresponding absorbance band is therefore observed in the near-UV region rather than in the visible region. Hence, these compounds are colorless, in marked contrast to the brilliant red or orange copper(I) species and the dark blue of the nickel(0) compound. A summary of these spectra appears in Table 1.

We have prepared and characterized zinc(II) complexes with dmphen, illustrating several similarities as well as significant differences between them and the previously described copper(I) species. The structure of [ZnNO$_3$(dmphen)$_2$]NO$_3$ (**1**) as determined by X-ray crystallography shows one nitrate to be coordinated to zinc. With this counterion, which can coordinate relatively strongly, zinc can expand its coordination sphere to give a five-coordinate structure as shown in Fig. 1. This coordinated nitrate appears to be dissociable in aqueous solution—^{1}H NMR and UV–vis spectra are essentially identical to those of **2**.

Figure 2 shows the structure of a tetrahedral Zn(dmphen)$_2^{2+}$ ion as it occurs in a crystal of Zn(dmphen)$_2$(BF$_4$)$_2$ (**2**). Note that with the very weakly coordinating tetrafluoroborate counterion a pseudotetrahedral ion is obtained, similar to those observed for the corresponding copper species described previously.

A brief summary of significant parameters from the X-ray crystallography work is shown in Table 2 and includes a comparison to the structure [1] of Cu(2,9-di-n-pentyl-1,10-phenanthroline)$_2^+$ ion **3**, of analogous pseudotetrahedral structure.

Comparison of the values in Table 2 shows that the length of zinc–nitrogen bonds in **2** is ~0.1 Å less than that of the copper–nitrogen bonds in the analogous copper system **3**. This is consistent with the smaller ionic radius [10] generally observed with zinc(II) in comparison to copper(I). In addition, the ability of the zinc to expand its coordination sphere, as in compound **1**, while seemingly inconsistent with its lesser size, is consistent with the greater Lewis acidity of zinc(II) over copper(I).

The preference, usually so pronounced for the copper compounds, for a 1 : 2 stoichiometry (metal to ligand) is not apparent with zinc. This information is obtained from the ^{1}H NMR spectra of the compounds, as shown in Fig. 3. The titration was performed under conditions where nitrate does not bind to the zinc (that is, nitrate is dissociated). From the integrals of these spectra, we obtained titration curves as shown in Fig. 4. These gave values of $1.47(\pm 0.28)\times 10^4$ M^{-1} and $1.52(\pm 0.62)\times 10^4$ M^{-1} for K_1 and K_2, respectively at 215 K. We observed that the ^{1}H NMR spectrum of this compound displayed broad peaks at room temperature, which became sharp as the sample was heated to 75°C. Thus, the high temperature apparently yields sharp signals consisting of time-averaged chemical shifts (data summarized in Table 1) for an exchange occurring rapidly on the NMR time scale, while in the low-temperature titration experiment the exchange processes slow sufficiently to observe separate species.

A comparison of these ^{1}H NMR results with those obtained for the corresponding copper(I) species is instructive. One would expect a substantial increase in observed inductive effect with zinc(II). The spectra

Table 1. Selected ^{1}H chemical shifts (ppm), UV–vis λ_{max} values (nm) and extinction coefficients (ε) for compounds **1** ([ZnNO$_3$(dmphen)$_2$]NO$_3\cdot$H$_2$O), **2** ([Zn(dmphen)$_2$](BF$_4$)$_2$), **3** ([Cu(dmphen)$_2$]·(CuCl$_2$)), **4** (Ni(dmphen)$_2$) and **6** ([Ag(dmphen)$_2$]BF$_4$). Solvents are as follows: **1** and **2**, H$_2$O; **3**, CH$_2$Cl$_2$; **4**, EtOH; **6**, CH$_3$CN

	1	**2**	**3**	**4**	**6**
Methyl group chemical shift	2.76	2.77	2.40	2.81	2.72
Phenanthroline bands (ε)	206(54,100)	206(43,900)	207(63,750)	204(36,300)	208(43,900)
	228(68,800)	230(75,100)	232(91,800)	232(71,100)	232(58,000)
	272(46,700)	272(52,600)	275(70,800)	270(48,900)	272(54,000)
Charge transfer bands (ε)	316(4,640)	316(5,510)	456(6,410)	456(200)	332(1,720)
	328(2,990)	330(3,170)	—	644(457)	348(826)

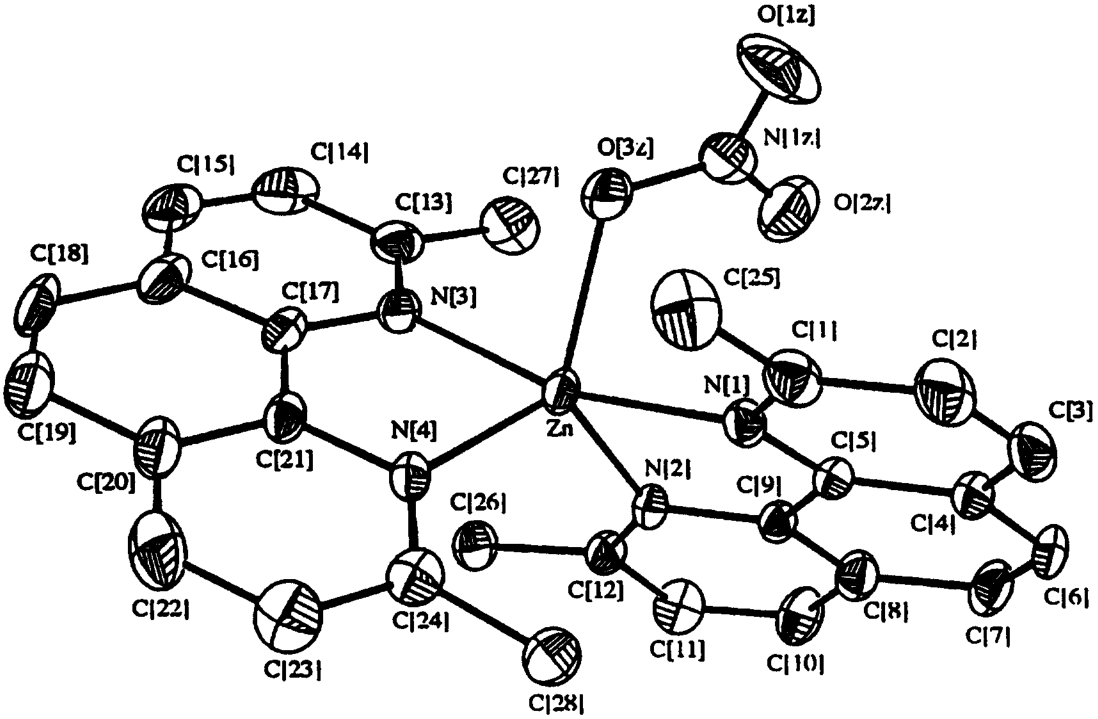

Fig. 1. Structure of **1** showing the five-coordinate geometry about the central zinc atom and the coordinated nitrate directly above the zinc.

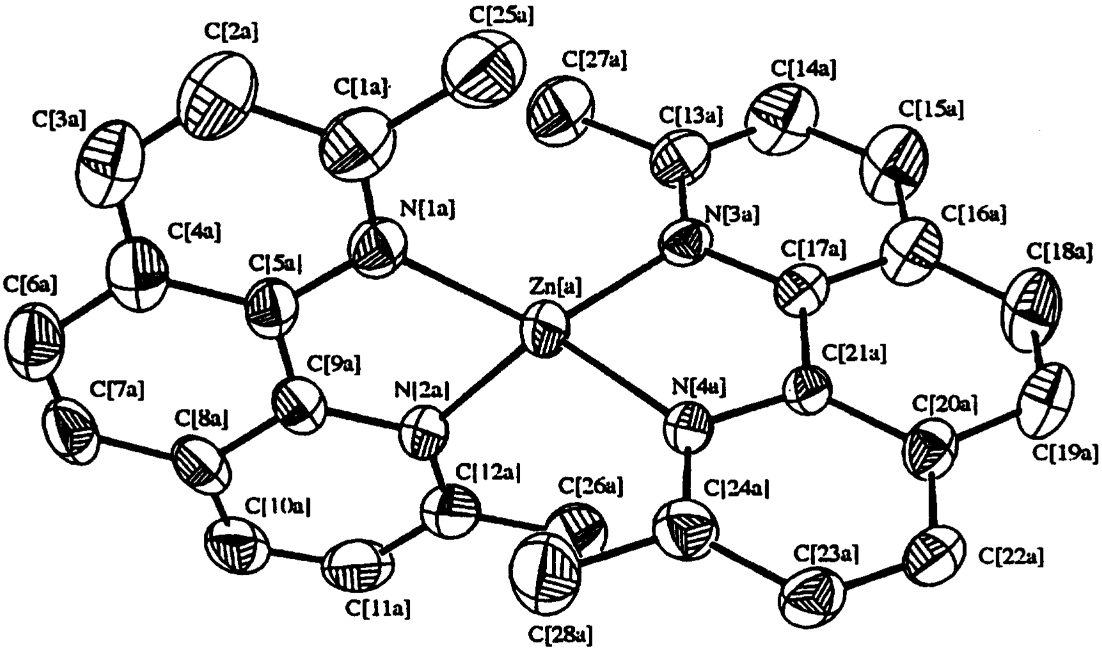

Fig. 2. Structure of the pseudotetrahedral $Zn^{II}(dmphen)_2$ ion in **2**.

show that the inductive effect of the zinc atom on the chemical shift of the dmphen methyl protons is ~0.28 ppm (the difference between the free and the 1 : 1 species). The analogous inductive effect in the copper species [1] is ~0.06 ppm. A similar comparison can be made regarding the ring-current effect of one aromatic ligand on another which arises from the magnetic anisotropy of the electrons of the π-system. This ring-current effect, which operates in the upfield direction, is shown to be 0.68 ppm from the spectra above, while the corresponding copper value is ~0.52 ppm. These observed differences are consistent with a system in

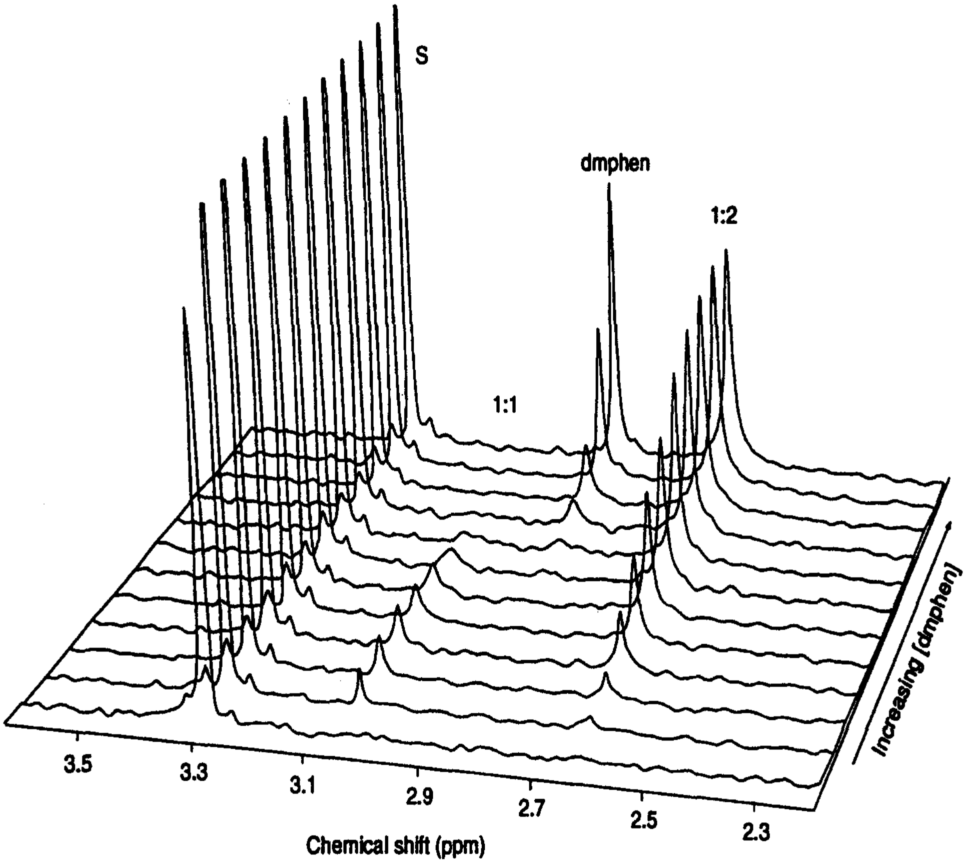

Fig. 3. 500 MHz ^{1}H NMR spectra (methyl region) for the titration of 5 mM $Zn(NO_3)_2$ with dmphen at 215 K in d_4-methanol/water (80 : 20). Peaks in the spectra correspond to the residual solvent (S) and the methyl protons of 1 : zinc dmphen complex, free dmphen and 1 : 2 zinc dmphen complex. The methyl protons of the 1 : 2 complex are shifted upfield relative to the free and 1 : 1 complex due to the ring current shift caused by the neighboring phenanthroline.

which the singly charged copper(I) is replaced with zinc(II). While an interaction transmitted through bonds, like the inductive effect, is likely to vary with the charge, an interaction transmitted through space, such as the magnetic anisotropy responsible for a ring-current shift, would be expected to vary only with the position of the atoms [11].

The preparation of the zinc complexes described above led us to demonstrate the generality of the d^{10} pseudotetrahedral structure by adding the nickel(0) complex **4** and the silver(I) complex **6** to this isoelectronic series. Thus, addition of 1/2 equiv. of *bis*(1,5-cyclooctadiene)nickel(0) to a solution of dmphen (2,9-dimethyl-1,10-phenanthroline) gave the navy blue nickel(0)(dmphen)$_2$ (**4**). In contrast to the zinc species, this nickel complex exhibits a charge transfer band of rather low energy (see Table 1). In other words, the energy of the *d* orbitals in these d^{10} species increases as expected as one looks to the left on the periodic table. This nickel compound also differs from the copper(I) and zinc(II) species in being highly air-sensitive, as one might expect for nickel in this oxidation state. Compound **4** exhibits the sharp ^{1}H and ^{13}C NMR resonances characteristic of diamagnetic species and is sufficiently stable to give a sharp melting point at nearly 300°C. The simplicity and absence of unexplained resonances in these spectra attest to the homogeneity of the material. Elemental analysis confirms this observation. In addition, the symmetry evident in the NMR spectra is consistent with the pseudotetrahedral structure expected with a tetrahedral enforcing ligand like dmphen. However, one is left to speculate on the electronic structure of the ground state for this compound and the degree to which electron density from the nickel is present in the dmphen aromatic system.

Although compound **4** is clearly crystalline, with beautiful rhombic morphology, our attempts to obtain X-ray diffraction data proved consistently fruitless. However, an attempt to recrystallize this material from dichloromethane gave, after a short time, a dramatic color change (to red) and eventual deposition of large amber crystals. These were not only amenable to X-ray diffraction (see Fig. 5), but were also easily isolated in pure (solvent free) and readily characterizable form. Thus, we were able to obtain mass spectra and elemental analysis, but not NMR spectra (this compound is paramagnetic). All

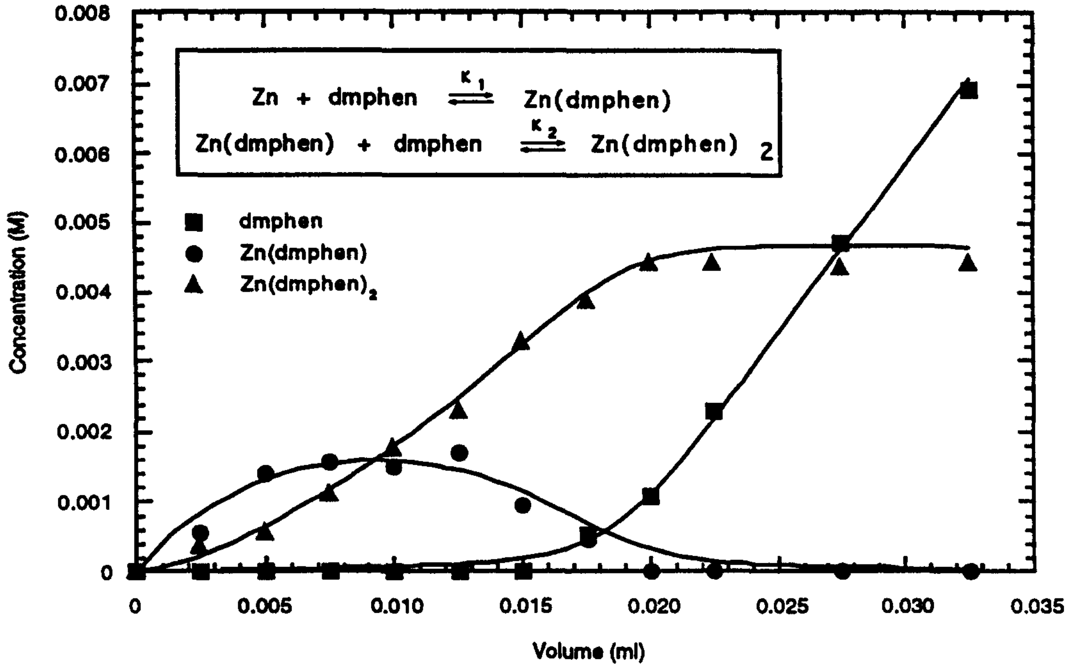

Fig. 4. Titration curves for the ^{1}H NMR data (215 K) shown in Fig. 3. Data points correspond to the normalized integrals of the methyl resonances, while the lines drawn through the points show the best fit of the titration data to the Zn^{2+}-dmphen equilibrium model shown in the inset. The regression analysis yielded equilibrium constants of $K_1 = 1.47(\pm 0.28) \times 10^4$ M^{-1} and $K_2 = 1.52(\pm 0.62) \times 10^4$ M^{-1}.

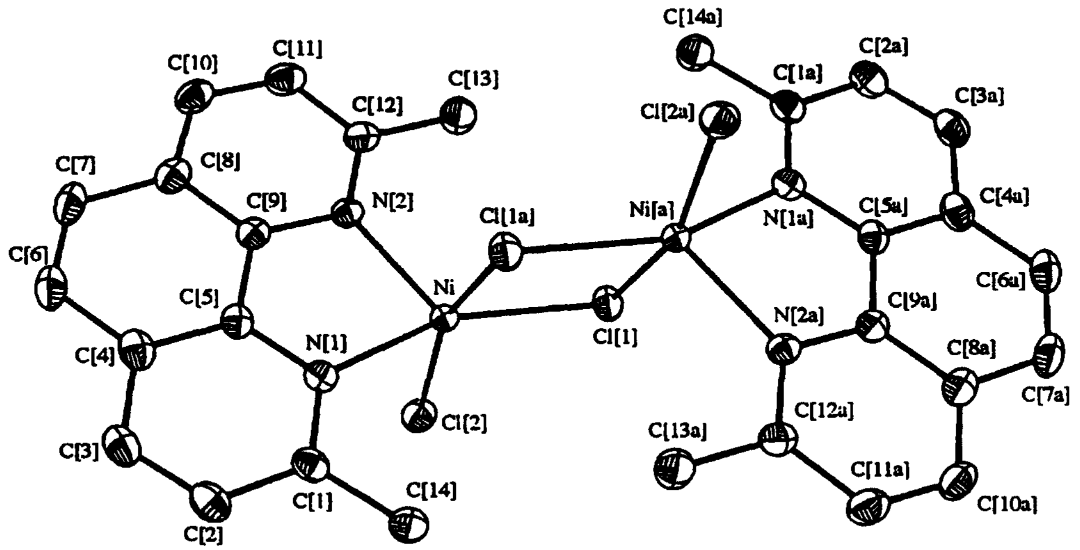

Fig. 5. Structure of di-μ-chloro-sym-*trans*-dichloro-bis-(dmphen) dinickel(II) (**5**).

of the data (see Table 2) we obtained indicated that the crystals were di-μ-chloro-sym-*trans*-dichloro-*bis*-(dmphen) dinickel(II) (**5**). Several reports are to be found in the literature of compounds that are closely related to **5** or may be **5**. This compound was first reported [12] as a dichloromethane solvate with a similar unit cell. In another report [13] a compound which appears to be **5** is shown with a different unit cell. However, neither of these reports provide details of isolation or characterization.

In what we believe to be the first extension to second-row transition metals of the structure exemplified by the compounds described above, we have prepared silver(I) *bis*-dmphen tetrafluoroborate (**6**) in an analogous manner. This colorless complex exhibits many of the structural features seen in the zinc and copper compounds, though with considerably longer bonds to the silver atom, as one might expect. Although this structure, shown in Fig. 6, shares many features with the first row compounds, it deviates

Table 2. Selected bond distances (Å) and angles (°) for compounds **1** ($[ZnNO_3(dmphen)_2]NO_3 \cdot H_2O \cdot CH_3CH_2OH$), **2** ($[Zn(dmphen)_2](BF_4)_2$), **3** ([Cu(2,9-di-*n*-pentyl-1,10-phenanthroline)$_2$], $CuCl_2$), **5** ($Ni_2(dmphen)_2Cl_2(\mu\text{-}Cl_2)$) and **6** ($[Ag(dmphen)_2]BF_4 \cdot CH_2Cl_2$)

	1	**2**	**3**	**5**	**6**
M—N distance	2.060(3)	1.991(4)–	2.156(4)	2.034(2)	2.308(4)–
	2.126(3)	2.034(4)	—	—	2.411(4)
M—X (NO_3 or Cl) distance	2.121(3)	—	—	2.309(1)	—
	—	—	—	2.388(1)	—
N—Zn—O angle	83.1(1)	—	—	—	—
	81.2(1)	—	—	—	—
	125.4(1)	—	—	—	—
	118.2(1)	—	—	—	—
N—M—N angle(s)[a]	80.4(1)–	83.6(1)–	82.4(2)	81.9(1)	72.2(2)
	80.6(1)	84.5(2)	82.9(4)	—	72.7(2)

[a] For these compounds, the angles given are for two nitrogens in the same phenanthroline system.

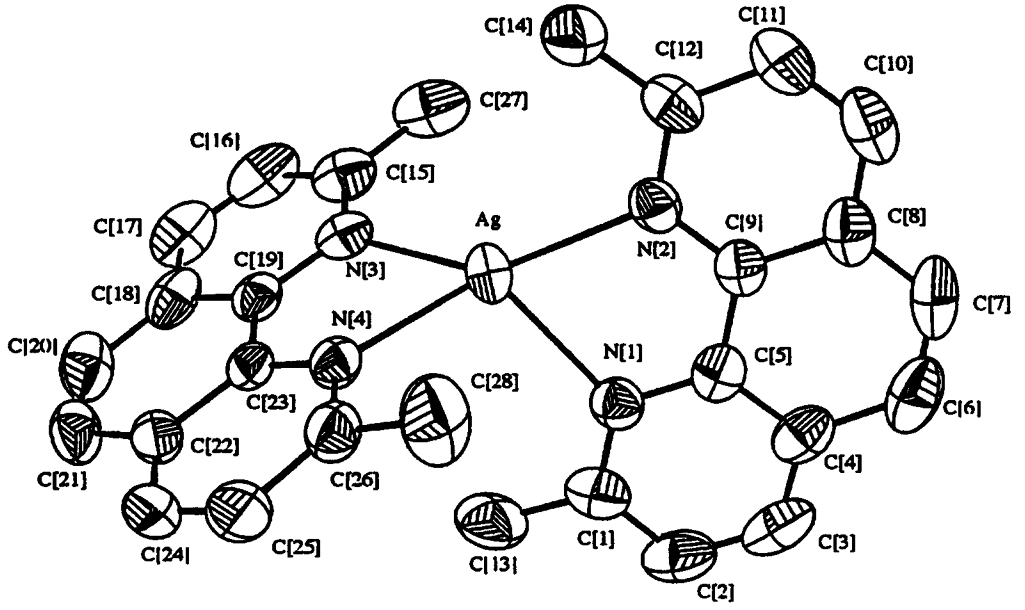

Fig. 6. Structure of Silver(I) bis-(dmphen) ion in **6** showing pseudotetrahedral geometry.

much more significantly from an ideal tetrahedral geometry, due, in part, to the added length of the bonds. Some critical bond lengths and angles are shown in Table 2.

The data presented here show that the isoelectronic series containing the familiar copper(I) dmphen complexes can be extended to include the nickel(0) compound **4**, zinc(II) compounds **1** and **2**, and silver(I) species **6**. Future efforts may eventually reveal the extent to which this series can be further extended.

EXPERIMENTAL

General experimental details

Melting point determinations are uncorrected. Tetrahydrofuran was distilled from potassium benzophenone ketyl immediately prior to use. Toluene, hexane and dichloromethane were either distilled from an appropriate drying agent or purchased in anhydrous form. Other reagents were used as received unless otherwise indicated. Flash chromatography was performed on Silica gel 60 (EM Science) according to the procedure of Still [14]. Air- and moisture-sensitive reactions were performed under nitrogen atmosphere using flame-dried glassware and standard methods for handling air sensitive reagents. Mass spectra were obtained using fast atom (Xe) bombardment ionization on a VG 70SEQ tandem hybrid spectrometer. UV–vis spectra were obtained with a Hewlett-Packard model 8452A diode array spectrophotometer.

Compounds for which X-ray analysis is reported were obtained as hydrates and/or solvates as indicated by nomenclature in the Experimental below. Each of these compounds, except compound **I** which retained one water of hydration, was freed of solvents upon vacuum drying. For this reason, all analytical data obtained for these compounds applies to solvent-free material. Formulae and names will include the appropriate solvents when referring to crystallographic matters while other information (such as Table 1, elemental analyses and spectra) will not include reference to solvents not present during analysis.

500 MHz ^{1}H NMR spectra used in the zinc titration (Figure 3) were acquired on a Bruker (AM-500) spectrometer at 215 K using d_4-methanol (Aldrich) : water (80 : 20) as solvent. Chemical shifts were referenced relative to the residual solvent methyl resonance at $\delta = 3.3$ ppm. Titrations were carried out by adding incremental amounts of a dmphen (Aldrich) stock solution (0.258 M) to 5 mM $Zn(NO_3)_2$ directly in the NMR tube. Molar concentrations of the $Zn(dmphen)^{2+}$, $Zn(dmphen)_2^{2+}$ and free dmphen were calculated from peak areas by using the area of the $Zn(dmphen)_2^{2+}$ resonance at the highest total dmphen concentration as a 5 mM standard after correcting for dilution. Nonlinear least-squares analysis [15, 16], was carried out using a custom program which calculated the best fit stepwise formation constants for the Zn(dmphen) equilibrium model (inset in Fig. 4).

X-ray crystallography

In each case a crystal of the compound was mounted on a glass fiber in oil and transferred to an Enraf–Nonius CAD-4 diffractometer operating with Mo-K_α radiation through a graphite crystal monochromator. Scan speeds were 1.0–7.5° min^{-1}. Extinction corrections were, when used, $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{1/4}$, where χ is given in Table 3. For the structures where the extinction correction was removed, no differences in bond lengths or angles were found. The structures of compounds of each compound were solved by direct methods using a public-domain program called XCAD4, with further work being carried out using the PC version of Siemens SHELXTL PLUS. Refinements were performed by a full-matrix least-squares method, with riding model, calculated isotropic U hydrogen atoms. Structures are presented in the form of 50% probability ellipsoids. Other information for each structure is given in Table 3.

$[ZnNO_3(dmphen)_2]NO_3 \cdot H_2O \cdot CH_3CH_2OH$ (**1**)

A solution of dmphen (4.53 g, 20.0 mmol) in methanol (20 cm^3) was added to a stirred solution of zinc nitrate hydrate (2.97 g, 10.0 mmol) in methanol (20 cm^3). A white precipitate formed immediately. This material was collected on a filter, washed with methanol and dried under vacuum to give 5.66 g (91%) of the monohydrate as a white solid. Recrystallization from aqueous ethanol gave the monohydrate monomethanolate as white plates suitable for X-ray analysis. Vacuum drying gave the monohydrate: M.pt 225.5–226°C; UV–vis $\lambda_{max}(H_2O)$: 206 ($\varepsilon = 54{,}100$ M^{-1} cm^{-1}), 228 ($\varepsilon = 68{,}800$), 272 ($\varepsilon = 46{,}700$), 316 (sh, $\varepsilon = 4{,}640$), 328 nm (sh, $\varepsilon = 2{,}990$); ^{1}H NMR (500 MHz, DMSO-d_6, 75°C): δ 8.7 (2H, br m), 8.1 (2H, br m), 7.9 (2H, br m), 2.76 (6H, s); MS m/z (relative intensity): 546 $[M(^{68}Zn)-(NO_3)^-]^+$ (7), 545 ($[M(^{67}Zn)-(NO_3)^-]^+$ (5), 544 $[M(^{66}Zn)-(NO_3)^-]^+$ (10), 542 $[M(^{64}Zn)-(NO_3)^-]^+$ (15), 334 (30), 209 (100); HRMS: calc. for $C_{28}H_{24}N_5O_3{}^{68}Zn$ [M less $(NO_3)^-]^+$ 546.1128, found 546.1108; calc. for $C_{28}H_{24}N_5O_3{}^{67}Zn$ [M less $(NO_3)^-]^+$ 545.1150, found 545.1136; calc. for $C_{28}H_{24}N_5O_3{}^{66}Zn$ [M less $(NO_3)^-]^+$ 544.1140, found 544.1119; calc. for $C_{28}H_{24}N_5O_3{}^{64}Zn$ [M less $(NO_3)^-]^+$ 542.1171, found 542.1138. Anal. Found: C, 54.15; H, 3.99; N, 13.46. Calc. for $C_{28}H_{26}N_6O_7Zn$: C, 53.90; H, 4.20; N, 13.47%.

$Zn(dmphen)_2(BF_4)_2$ (**2**)

A solution of dmphen (4.53 g, 20.0 mmol) in methanol (20 cm^3) was added to a stirred solution of zinc tetrafluoroborate hydrate (3.65 g, 10.0 mmol) in methanol (20 cm^3). A white precipitate formed immediately. This material was collected on a filter, washed with methanol and dried under vacuum to give 5.63 g (91%) of a white solid. Recrystallization from aqueous ethanol gave white plates: M.pt >350°C; UV–vis: λ_{max} (H_2O) 206 ($\varepsilon = 43{,}900$ M^{-1} cm^{-1}), 230 ($\varepsilon = 75{,}100$), 272 ($\varepsilon = 52{,}600$), 316 (sh, $\varepsilon = 5{,}510$), 330 nm (sh, $\varepsilon = 3{,}170$); ^{1}H NMR (500 MHz, DMSO-d_6, 75°C): δ 8.68 (2H, br d, $J = 8.1$ Hz), 8.09 (2H, s), 7.87 (2H, d, $J = 8.2$ Hz), 2.77 (6H, s); MS m/z (relative intensity) 567 $[M(^{68}Zn)\text{-}(BF_4)^-]^+$ (25), 501 (45), 499 (65), 481 (65), 479 (65), 399 (70), 397 (100); HRMS: calc. for $C_{28}H_{24}BF_4N_4{}^{64}Zn$ [M less $(BF_4)^-]^+$ 567.1322, found 567.1314. Anal. Found: C, 50.74; H, 3.74; N, 8.39. Calc. for $C_{28}H_{24}B_2F_8N_4Zn$: C, 51.30; H, 3.69; N, 8.55%.

$Ni(dmphen)_2$ (**4**)

In the glovebox (this reaction can be performed on a manifold as well), a suspension of bis(1,5-cyclooctadiene)nickel(0) in tetrahydrofuran (40 cm^3) was added to a solution of dmphen (3.29 g, 14.5 mmol) in tetrahydrofuran (20 cm^3) at room temperature. This produced immediate dissolution of the reactants and dark, virtually black, color. After about 1 h, much of the dark material had precipitated. The result was similar using ethanol as solvent. This material was collected on a filter and dried under vacuum to give (3.1 g, 90%) of the nickel(0) complex as a black solid. A sample for elemental analysis was obtained by recrystallization from toluene: M.pt 290–295°C; UV–vis: λ_{max} (CH_3CH_2OH) 204 ($\varepsilon = 36{,}300$ M^{-1} cm^{-1}), 232 ($\varepsilon = 71{,}100$), 270 ($\varepsilon = 48{,}900$), 458 ($\varepsilon = 200$), 644 nm ($\varepsilon = 457$); ^{1}H NMR (500 MHz, CH_3CN-d_3): δ

Table 3. Crystallographic data for compounds **1** ([ZnNO$_3$(dmphen)$_2$]NO$_3$·H$_2$O·CH$_3$CH$_2$OH), **2** ([Zn(dmphen)$_2$](BF$_4$)$_2$·2H$_2$O), **5** (Ni$_2$(dmphen)$_2$Cl$_2$(μ-Cl$_2$)·CH$_2$Cl$_2$) and **6** ([Ag(dmphen)$_2$]BF$_4$·CH$_2$Cl$_2$)

	1	2	5	6
Formula	$C_{30}H_{32}N_6O_8Zn$	$C_{28}H_{28}B_2F_8N_4O_2Zn$	$C_{29}H_{26}Cl_6N_4Ni_2$	$C_{29}H_{26}AgBCl_2F_4N_4$
fw	670.0	691.6	758.6	696.1
Color	Clear	Pale yellow	Amber	Yellow
Habit	Plate	Fragment	Block	Plate
Dimensions (mm)	0.08 × 0.36 × 0.36	0.15 × 0.25 × 0.36	0.24 × 0.26 × 0.30	0.15 × 0.30 × 0.35
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z	4	4	2	2
a (Å)	11.385(2)	13.400(3)	10.631(2)	10.711(2)
b (Å)	15.440(3)	13.430(3)	13.406(2)	11.285(2)
c (Å)	17.475(3)	16.430(3)	11.787(2)	13.275(3)
α (°)		87.90(3)	—	65.36(3)
β (°)	106.37(3)	81.20(3)	97.68(2)	73.27(3)
γ (°)		87.70(3)	—	70.84(3)
V (Å^3)	2947.3(15)	2918(1)	1664.8(8)	1356.2(5)
μ (mm^{-1})	0.896	0.928	1.638	0.996
min/max transm	1.000/0.991	0.967/0.913	0.8422/0.9942	0.967/0.922
2θ range (°)	2.0–50.0	2.0–50.0	2.0–50.0	2.0–50.0
Index ranges	$0 \leqslant h \leqslant 13$	$0 \leqslant h \leqslant 15$	$0 \leqslant h \leqslant 12$	$0 \leqslant h \leqslant 12$
	$-1 \leqslant k \leqslant 18$	$-15 \leqslant k \leqslant 15$	$-2 \leqslant k \leqslant 15$	$-12 \leqslant k \leqslant 13$
	$-20 \leqslant l \leqslant 19$	$-19 \leqslant l \leqslant 19$	$-13 \leqslant l \leqslant 13$	$-15 \leqslant l \leqslant 13$
$F(000)$	1392	1408	768	700
χ, extinction correction	N/A	N/A	0.0010(2)	N/A
ρ_{calcd} (g cm^{-1})	1.366	1.574	1.513	1.705
T (K)	183	183	183	183
λ (Å)	0.71073	0.71073	0.71073	0.71073
No. of unique reflections	4949	10237	2919	4626
No. of obsd reflections	3419	6451	2487	3036
GOF	1.04	1.19	1.01	1.19
Absorption correction	Semiempirical	Empirical	Empirical	Semiempirical
Δ/δ (max), (mean)	0.091, 0.037	0.004, 0.000	0.010, 0.001	0.012, 0.001
R^a (%)	4.55	5.42	2.90	4.72
$R_w{}^b$ (%)	7.43	7.85	4.87	8.31

[a] $R = \Sigma(F_o - F_c)/\Sigma F_o$.

[b] $R_w = \Sigma[w^{1/2}(F_o - F_c)]/[\Sigma w^{1/2} F_o]$.

8.22 (2H, d, $J = 8.1$ Hz), 7.79 (2H, s), 7.55 (2H, d, $J = 8.1$ Hz), 2.81 (6H, s); ^{13}C NMR (125 MHz, CH$_3$CN-d_3): δ 159.6, 146.3, 137.3, 127.9, 126.5, 124.2, 25.5; MS *m/z* (relative intensity) 476 [M$^+$(^{60}Ni)] (10), 474 [M$^+$(^{58}Ni)] (20), 268 (20), 266 (45), 209 (100); HRMS calcd for $C_{28}H_{24}N_4{}^{58}Ni$ (M$^+$) 474.1354, found 474.1337; calc. for $C_{28}H_{24}N_4{}^{60}Ni$ (M$^+$) 476.1309, found 476.1307. Anal. Found: C, 70.85; H, 5.24; N, 11.74. Calc. for $C_{28}H_{24}N_4Ni$: C, 70.77; H, 5.09; N, 11.79%.

Ni$_2$(dmphen)$_2$Cl$_2$(μ-Cl$_2$)·CH$_2$Cl$_2$ (5)

Nickel(0) (dmphen), **4** (250 mg, 0.526 mmol) was dissolved in dichloromethane (20 cm^3), initially giving a solution of dark blue color, characteristic of the starting nickel(0) species. After 2 h, the solution turned red. Amber crystals, suitable for X-ray crystallography, formed on standing overnight. This material was collected on a filter and dried under vacuum to give 117.4 mg (66%) of the dimeric solvent free complex as a tan solid: M.pt >350°C; MS *m/z* (relative intensity) 643 (5), 641 (7), 639 (10), 637 (5), 511 (5), 509 (5), 434 (5), 432 (10), 303 (75), 301 (100), 266 (55), 209 (10); HRMS calc. for $C_{28}H_{24}{}^{35}Cl_3N_4{}^{58}Ni_2$ (M$^+$ less Cl) 636.9773, found 636.9765; calc. for $C_{28}H_{24}{}^{35}Cl_2{}^{37}ClN_4{}^{58}Ni_2$ 638.9744, calc. for $C_{28}H_{24}{}^{35}Cl_3N_4{}^{58}Ni{}^{60}Ni$ 638.9728, found 638.9747; calc. for $C_{28}H_{24}{}^{35}Cl_2{}^{37}ClN_4{}^{58}Ni{}^{60}Ni$ 640.9698, calc. for $C_{28}H_{24}{}^{35}Cl_3N_4{}^{58}Ni{}^{62}Ni$ 640.9703, found 640.9711. Anal. Found: C, 49.71; H, 3.73; N, 8.03; Cl, 20.92. Calc. for $C_{28}H_{24}Cl_4N_4Ni_2$: C, 49.77; H, 3.58; N, 8.29; Cl, 20.99%.

Ag(dmphen)$_2$BF$_4$·CH$_2$Cl$_2$ (6)

Silver(I) tetrafluoroborate (10.00 g, 51.37 mmol) was added to a stirred solution of dmphen hydrate (23.26 g, 102.8 mmol) in dichloromethane (250 cm^3) at room temperature. The resulting suspension was stirred for 72 h. The solid material was removed by filtration and washed repeatedly with dichloromethane. Methanol (25 cm^3) was added and the combined filtrate and washings, an amber solution, was heated to boiling and solvent was allowed to distil away until the volume was reduced to ~ 100 cm^3. Slow cooling of this material gave crystals for the solvate suitable for X-ray analysis. The material not used for this purpose was collected on a filter and dried under vacuum to give 3.27 g (10%) of the complex as white crystals. Recrystallization of a 500 mg sample of this material from acetonitrile/water gave 281.7 mg of the solvent-free complex as a white crystalline solid: M.pt 354–355°C; UV–vis: λ_{max} (CH_3CN) 208 ($\varepsilon = 43{,}900$ M^{-1} cm^{-1}), 232 nm ($\varepsilon = 58{,}000$), 272 ($\varepsilon = 54{,}000$), 292 (sh, $\varepsilon = 26{,}400$), 316 (sh, $\varepsilon = 2740$), 332 ($\varepsilon = 1{,}720$), 348 nm ($\varepsilon = 826$); ^1H NMR (500 MHz, DMSO-d_6): δ 8.71 (2H, d, $J = 8.3$ Hz), 8.16 (2H, s), 7.95 (2H, d, $J = 8.31$ Hz), 2.72 (6H, s); MS m/z (relative intensity) 525 $[M(^{109}Ag)-(BF_4)^-]^+$ (55), 523 $[M(^{107}Ag)-(BF_4)^-]^+$ (60), 317 (95), 315 (100), 209 (10); HRMS calc. for $C_{28}H_{24}{}^{109}AgN_4$ (M^+ less BF_4) 525.1049, found 525.1038; calc. for $C_{28}H_{24}{}^{107}AgN_4$ (M^+ less BF_4) 523.1052, found 523.1027. Anal. Found: C, 54.97; H, 4.04; N, 9.65. Calc. for $C_{28}H_{24}AgBF_4N_4$: C, 55.02; H, 3.96; N, 9.17%.

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