Unfortunately, because of the presumed UV-vis and IR spectral similarities between **1** and $Cr(CO)_5(dmbpy)$, it was not possible to unambiguously identify the latter in the reaction mixtures and to separate the individual rate constants for the dissociation of either **1** or $Cr(CO)_5(dmbpy)$. Nevertheless, we are aware that $Cr(CO)_5(dmbpy)$ may be present in significantly high stationary concentrations, particularly in those experiments where large amounts of free dmbpy ligand were added.[18] Therefore, the significance of the k_{obs} values obtained under the various conditions described above is ambiguous at the present stage. Further experiments with various concentrations of CO and dmbpy are necessary in order to obtain kinetic data from which the individual rate constants of all the processes in eq 6a,b can be obtained.

Concluding Remarks

To our knowledge a dinuclear complex of type **1** has not been considered previously to be involved in the formation of group 6 $M(CO)_4(L\text{-}L)$ chelate complexes with 1,4-diazadiene type ligands. Moreover, **1** appears to be the first example of a complex in which such a ligand acts as a bridge between two separate transition-metal centers. Naturally the question arises whether or not the formation and isolation of **1** is a unique case in this context. We are currently extending our studies to other, related, chelating ligands and to the analogous molybdenum and tungsten compounds in order to clarify this point.

A plausible explanation for the high-yield isolation of **1** is that its precipitation from pentane solution, owing to the low solubility in that solvent, drives the equilibrium of eq 6a to the left side. Beyond this it seems possible that upon coordination of one $Cr(CO)_5$ unit to the dmbpy ligand the coordinating ability of the second pyridine ring is enhanced. It is worthwhile to mention in this context that in some cases of polydentate N-donor heteroaromatic ligands it was found difficult to obtain only partly coordinated complexes because of the propensity of such ligands toward complexation of all available coordination sites.[19] However, on the other hand it has to be noted that in complex **1**, as shown by the X-ray diffraction structure analysis[16] of the crystalline material, the two pyridine rings are twisted by ca. 90° relative to each other, which prevents any interaction through the π system. Thus, provided that this structural feature is maintained in solution, mutual influence between the two halves of complex **1** should be restricted to through-space interactions and to transmission through the σ system of the dmbpy ligand.

Registry No. **1**, 120360-44-3; **2**, 15740-68-8; dmbpy, 1134-35-6; $Cr(CO)_5(\eta^2\text{-}(Z)\text{-cyclooctene})$, 92889-73-1; $Cr(CO)_6$, 13007-92-6; CO, 630-08-0.

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(18) Comparing the IR spectral changes displayed in Figures 1B and 2, we note that in the latter case the splitting of the strong bands at 1937 and 1921 cm^{-1} is not maintained throughout but that a band at an intermediate position emerges. This observation may be taken as pointing toward the presence of $Cr(CO)_5(dmbpy)$ in which, by analogy with the model compound $Cr(CO)_5$(2-phenylpyridine),[2] the E-mode degeneracy could perhaps be preserved.

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New Pathway to Heterodinuclear Complexes with Equivalent Coordination Sites: Application of the Cis-Trans Isomerization of the Oxamido Group

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There are several research fields in which it would be advantageous to have a series of well-characterized mixed-metal complexes. From a literature survey, it appears that there are mainly two types of ligands that can simultaneously coordinate two metal ions. In the first type the two coordination sites are equivalent, while they are inequivalent in the second. The coordination site inequality favors the formation of mixed-metal complexes and a large majority of the known heterodinuclear complexes have been obtained in this way; the most frequent situation involves N_2O_2 and O_4 coordination sites.[1-3] To our knowledge, only two series of heterodinuclear complexes with identical coordination sites for both metal ions have been prepared so far. In the first case,[4] mononuclear complexes of β,δ-triketones or β-ketophenols have been used as ligands toward a second metal ion to yield heterodinuclear compounds. The interest of this strategy is limited by the instability of the mononuclear precursors, which very often transform into the related homodinuclear species even at room temperature. The second series[5,6] involves the Robson macrocyclic binucleating ligand, which offers equivalent N_2O_2 coordination sites to both metal ions. These heterodinuclear complexes (Cu(II)/M(II) with M = Mn, Co, Fe) have been prepared by a stepwise synthesis that includes a dinuclear intermediate with dissimilar surroundings for the metal ions. The coordination site equality is achieved by a modification of the ligand in the last step of the synthesis.

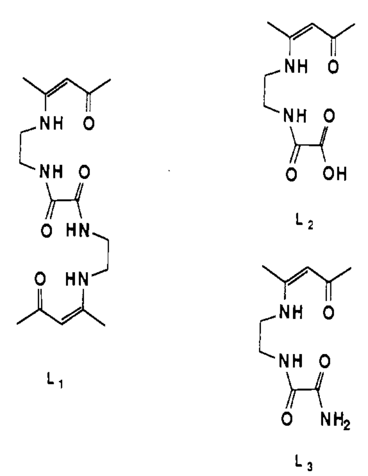

Figure 1. Ligands.

In the present paper we report on a new ligand, *N,N'*-bis(4-methyl-5-aza-3-hepten-2-on-7-yl)oxamide (L_1; cf. Figure 1), which can be isolated in the free state and then reacted with a copper ion to yield a mononuclear complex, $[Cu(L_1\text{-}3H)]^-$, which is able to act as a ligand toward a second divalent ion M^{2+} to yield a heterodinuclear species $Cu(L_1\text{-}4H)M$ (L_1-3H and L_1-4H representing the tri- and tetradeprotonated forms of L_1, respectively).

The possibility of preparing a mixed-metal complex with equivalent surrounding for both metal ions from a preformed symmetrical binucleating ligand is unexpected. It relies on the possibility of changing the conformation (cis vs trans) of the oxamido group. Indeed we could demonstrate that in the mononuclear species the copper ion is actually surrounded by three nitrogen and one oxygen atoms while both metals have N_2O_2 surrounding in the mixed-metal (Cu/Ni) complex.

Experimental Section

Ligand L_1. To a stirred solution of diethyl oxalate (2.6 g, 17.6 mmol) in CH_2Cl_2 (50 cm^3) was added AEH,[7] 7-amino-4-methyl-5-aza-3-hep-

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ten-2-one (5 g, 35.2 mmol). The solution was refluxed for 15 min. After the mixture was cooled, the white precipitate that appeared was filtered and dried (5.8 g, 97%). Anal. Calcd for $C_{16}H_{26}N_4O_4$: C, 56.8; H, 7.7; N, 16.6. Found: C, 56.4; H, 7.8; N, 16.4.

Complexes. $NaCu(L_1\text{-}3H)\cdot 2H_2O$. To L_1 (0.5 g, 1.48 mmol) suspended in MeOH (50 cm^3) was added an aqueous solution (10 cm^3) of NaOH (0.23 g). Copper chloride dihydrate (0.25 g, 1.48 mmol) in water (10 cm^3) was added dropwise with stirring, bringing about the dissolution of the ligand and the appearance of a pink solution. One hour later, the solution was filtered and evaporated. The precipitate was dissolved in CH_2Cl_2. Addition of pentane to the concentrated solution of CH_2Cl_2 yielded a pink precipitate, which was filtered and dried. (60% yield). Anal. Calcd for $C_{16}H_{27}CuN_4NaO_4$: C, 42.0; H, 5.9; Cu, 13.9; N, 12.2. Found: C, 41.5; H, 5.7; Cu, 13.6; N, 12.1.

$Cu(L_1\text{-}4H)Ni$. To $NaCu(L_1\text{-}3H)\cdot 2H_2O$ (0.2 g, 0.4 mmol) dissolved in water (20 cm^3) was added $Ni(OAc)_2\cdot 4H_2O$ (OAc = acetate) (0.11 g, 0.4 mmol) at once. The brown precipitate, which appeared very quickly, was filtered, washed with MeOH and Et_2O, and dried. Anal. Calcd for $C_{16}H_{22}CuN_4NiO_4$: C, 42.1; H, 4.8; Cu, 13.9; N, 12.3; Ni. 12.7. Found: C, 41.9; H, 4.8; Cu, 13.6; N, 12.2; N, 12.5.

Addition of $Cu(OAc)_2\cdot H_2O$ instead of $Ni(OAc)_2\cdot 4H_2O$ yielded $Cu(L_1\text{-}4H)Cu$. Anal. Calcd for $C_{16}H_{22}Cu_2N_4O_4$: C, 41.6; H, 4.8; Cu, 27.5; N, 12.1. Found: C, 41.7; H, 4.7; Cu, 27.1; N, 12.1. This compound was also obtained by mixing together L_1 and $Cu(OAc)_2\cdot H_2O$ in MeOH, as described elsewhere.[8] Using $Ni(OAc)_2\cdot 4H_2O$ instead of $Cu(OAc)_2\cdot H_2O$ yielded $Ni(L_1\text{-}4H)Ni$. Anal. Calcd for $C_{16}H_{22}N_4Ni_2O_4$: C, 42.7; H, 4.9; N, 12.4; Ni, 25.8. Found: C, 42.5; H, 5.0; N, 12.3; Ni, 25.6.

Until now, we could not obtain crystals of any of these compounds suitable for X-ray structure determination.

Microanalyses were performed by the Service Central du CNRS, Lyon, France. Visible spectra were recorded by using a Varian Cary 2300 spectrophotometer. Magnetic susceptibility data were collected on powdered samples with use of a Faraday-type magnetometer using mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C, 16.44 × 10^{-6} cm^3 mol^{-1}) as standard susceptibility. Data were corrected for diamagnetism of the ligand (estimated at −182 × 10^{-6} cgsu) and for temperature independent paramagnetism (TIP). EPR spectra were recorded at the X-band frequency (9.4–9.5 GHz) with a Bruker 200 TT spectrometer.

Discussion

In a previous paper,[8] we have described the complexing ability of the ligands L_1, L_2, and L_3. As expected on the basis of its symmetrical structure, the ligand L_1 reacts readily with copper(II) or nickel(II) ions to afford homodinuclear complexes $M(L_1\text{-}4H)M$, whatever mole ratio of reactants is used. This contrasts with the behavior of L_2, *N*-(4-methyl-5-aza-3-hepten-2-on-7-yl)oxamic acid, and L_3, *N*-(4-methyl-5-aza-3-hepten-2-on-7-yl)oxamide, which, in spite of their similarity to L_1, react with copper or nickel ions in the absence of a deprotonating reagent to yield trinuclear species, $M_3(L_2\text{-}3H)_2$ and $M_3(L_3\text{-}3H)_2$. However, addition of sodium hydroxide to the reaction mixture before the addition of metal ions causes the formation of the anionic mononuclear species $[M(L_i\text{-}3H)]^-$ ($M = Ni^{2+}$ or Cu^{2+}; i = 2, 3), which, according to NMR and EPR data, contain respectively a MN_2O_2 (i = 2) chromophore and a MN_3O (i = 3) chromophore. Considered together, these two sets of data suggest that, under suitable conditions, L_1 may behave similarly to L_2 and L_3 in giving mononuclear entities.

Actually, by slowly adding copper acetate (1 mol) to a mixture of L_1 (1 mol) and NaOH (4 mol), we succeeded in isolating a pink species that, according to analytical data, has to be formulated $NaCu(L_1\text{-}3H)\cdot 2H_2O$. In accordance with its anionic nature, this complex is readily soluble in water and aqueous solutions may be used to perform the second step of the reaction, i.e. the formation of a neutral dinuclear complex $Cu(L_1\text{-}4H)M$ (M = Cu, Ni), which, being insoluble in water, precipitates. Extension of this reaction to other metallic ions (M = Co, Mn, Fe) is in progress. At this stage, it may be noted that the related nickel complex $[Ni(L_1\text{-}3H)]^-$ has not been isolated.

To illustrate the main features of this synthetic pathway, i.e. the possibility of isolating a stable, well-identified mononuclear complex from a symmetrical potentially binucleating ligand and the possibility of adding a second metal ion to this ligand, we have focused our attention on the following species: $[Cu(L_1\text{-}3H)]^-$, $Cu(L_1\text{-}4H)Ni$, and $Cu(L_1\text{-}4H)Cu$. The data pertinent to the discussion of these two points are given in Table I. The introduction of a diamagnetic metallic ion at the second site of complexation makes easier the study of the heterobimetallic complex. So magnetic and EPR results give direct information concerning the paramagnetic center and allow a straightforward comparison with the $NaCu(L_1\text{-}3H)\cdot 2H_2O$ complex.

Table I. EPR and Visible Data with Absorption Coefficients in Parentheses

compd	color	EPR g_{iso}	EPR A_{iso}, G	EPR A_N, G	visible, nm
$NaCu(L_1\text{-}3H)\cdot 2H_2O$	pink	2.086	92	13.5	504 (120)
$Cu(L_1\text{-}4H)Cu$	violet	2.089			560 (270)
$Cu(L_1\text{-}4H)Ni$	brown	2.100	80	13.2	560 (130), 450 (220)
$Ni(L_1\text{-}4H)Ni$	red				452 (460)

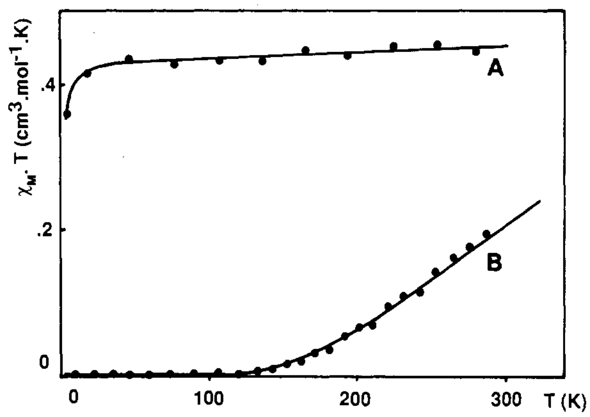

Figure 2. Experimental (●) and calculated (—) temperature dependences of χ_MT for $Cu(L_1\text{-}4H)Ni$ (A) and $Cu(L_1\text{-}4H)Cu$ (B). The equation of the calculated curve is $\chi_MT = (2N\beta^2g^2/k)[3 + \exp(-J/kT)]^{-1}(1 - p) + (N\beta^2g^2/k)p + \chi_{cor}T$, with $J = -2.25$ cm^{-1}, g = 2.11, and p = 0 for A and $J = -550$ cm^{-1}, g = 2.12, and p = 0.002 for B.

As does an original sample[8] prepared by reacting an excess of Cu^{2+} ions with L_1, the dinuclear complex $Cu(L_1\text{-}4H)Cu$ resulting from the present two-step synthesis displays a thermal variation of its magnetic susceptibility characteristic of a strong antiferromagnetic interaction ($J = -550$ cm^{-1}). This contrasts with, on the one hand, the diamagnetism of the related dinickel complex and, on the other hand, the Curie-like behavior of $[Cu(L_1\text{-}3H)]^-$ (C = 0.39 cm^3 mol^{-1} K, Θ = −0.5 K) and of $Cu(L_1\text{-}4H)Ni$ (C = 0.42 cm^3 mol^{-1} K, Θ = −3 K) (cf. Figure 2). The nonzero Θ value that characterizes $NaCu(L_1\text{-}3H)\cdot 2H_2O$ is suggestive of a feeble antiferromagnetic interaction ($J \leq -1$ cm^{-1}). It may be recalled that a Θ value of the same magnitude (i.e. −0.55 K) has been observed for $NaCu(L_2\text{-}3H)\cdot 1.33H_2O$ and attributed to a slight interaction between copper atoms in agreement with a structural determination.

Indeed the structural study of $NaCu(L_2\text{-}3H)\cdot 1.33H_2O$[8] shows that the sodium atoms and the water molecules play an important part in stabilizing the structure since they are simultaneously bonded to atoms belonging to different unit cells, with the net result of short distances, from 3.441 (1) to 3.786 (1) Å, between copper atoms of different $Cu(L_2\text{-}3H)^-$ anionic entities.

In the case of $Cu(L_1\text{-}4H)Ni$, the product χ_MT remains nearly constant from 300 to ca. 20 K. The χ_MT value of 0.42 cm^3 mol^{-1} K is as expected for an isolated copper ion (g = 2.11) and shows that the nickel ion does not contribute to the paramagnetism. Furthermore, this behavior proves that the sample is a genuine heterodinuclear complex and not a mixture of the two related homodinuclear complexes since such a mixture would be devoid of any paramagnetism below 100 K. The slight decrease of χ_MT at low temperature is likely attributable to a feeble intermolecular coupling ($J = -2.25$ cm^{-1}).

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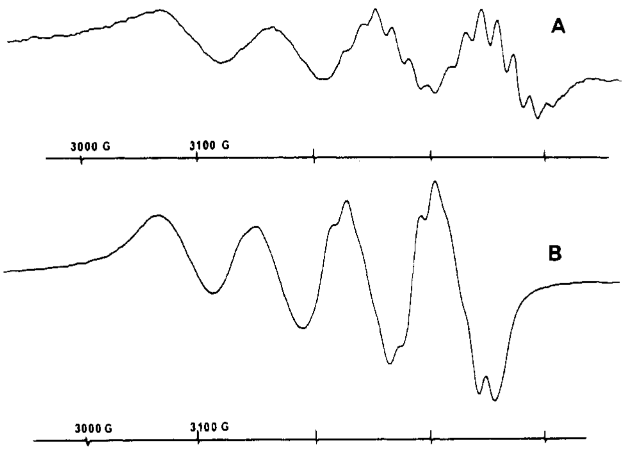

Figure 3. EPR spectra of $NaCu(L_1\text{-}3H)\cdot 2H_2O$ (A), $Cu(L_1\text{-}4H)Ni$ (B) complexes at room temperature.

Evidence that isomerization occurs upon addition of a second metal center is provided by EPR and electronic spectroscopies. Theoretically, EPR offers an easy means to determine the number of nitrogen atoms adjacent to the copper ion through the observation of the superhyperfine (shf) lines resulting from the interaction of the electron with the ^{14}N nuclei (I = 1).[9]

The isotropic spectra (solutions studied at room temperature) of $[Cu(L_1\text{-}3H)]^-$ and $Cu(L_1\text{-}4H)Ni$ show the well-known hyperfine structure of four lines due to coupling of the electron with the nuclear spin ($I = {}^3/_2$) of the copper atom and, in addition, a superhyperfine structure clearly discernible on the high-field components of the hyperfine spectrum (cf. Figure 3).

In the case of $[Cu(L_1\text{-}3H)]^-$, seven shf lines are observed with a separation of 13.5 G, indicating that the environment of the copper ion is N_3O, while for $Cu(L_1\text{-}4H)Ni$, the number of shf-lines decreases to five (separation of 13.2 G) in accordance with the presence of a CuN_2O_2 chromophore. Due to the occurrence of a strong antiferromagnetic coupling, the spectrum of $Cu(L_1\text{-}4H)Cu$ displays a broad signal devoid of any structure and centered at g = 2.089.

The change of conformation of the oxamido group in going from the mononuclear complex to the dinuclear complex is further supported by electronic spectra. Indeed the maximum of absorption (λ_{max}) suffers a significant shift from ca. 504 nm for the mononuclear species, $[Cu(L_1\text{-}3H)]^-$ and $[Cu(L_3\text{-}3H)]^-$, to ca. 560 nm for the dinuclear complexes, $Cu(L_1\text{-}4H)Cu$ and $Cu(L_1\text{-}4H)Ni$. This is in accordance with the change in the coordination spheres established by EPR data and the generally accepted assumption that a shift of λ_{max} toward shorter wavelengths is associated with an increase of the nitrogen atoms adjacent to the metal centers.[10] Interestingly, identical visible spectra (λ_{max} = 450 nm) are observed for the nickel chromophores in $Cu(L_1\text{-}4H)Ni$ and $Ni(L_1\text{-}4H)Ni$.

As suggested by a reviewer, the word mononuclear could be misused in the case of $NaCu(L_1\text{-}3H)\cdot 2H_2O$ since this complex could actually display a higher nuclearity. As previously mentioned this possibility would be supported by the presence of a feeble antiferromagnetic interaction as in $NaCu(L_2\text{-}3H)\cdot 1.33H_2O$. A structural study would be necessary, but we have not been able to prepare crystals suitable for such a work. Nevertheless, the main conclusion of this work, the N_3O environment of the copper atom in the anionic entity $Cu(L_1\text{-}3H)^-$ and the N_2O_2 environment in $Cu(L_1\text{-}4H)Cu$ and $Cu(L_1\text{-}4H)Ni$ is not called into question by the absence of structural determination.

Finally, converging arguments gained from spectroscpic data support the view that, in spite of its symmetrical structure, the ligand L_1 can be used to prepare heterodinuclear complexes involving two equivalent N_2O_2 coordination sites. This is realized via the isolation of a stable mononuclear copper complex with a CuN_3O chromophore and subsequent reaction with a second metal ion.

Registry No. $NaCu(L_1\text{-}3H)$, 120206-19-1; $Cu(L_1\text{-}4H)Cu$, 120206-20-4; $Cu(L_1\text{-}4H)Ni$, 120206-21-5; $Ni(L_1\text{-}4H)Ni$, 120206-22-6; diethyl oxalate, 95-92-1; 7-amino-4-methyl-5-aza-3-hepten-2-one, 89376-43-2; *N*,*N'*-bis(4-methyl-5-aza-3-hepten-2-on-7-yl)oxamide, 120206-18-0.

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Surprisingly High Stability of Alkali-Metal Complexes of the Ligand Tris(2-pyridylmethyl)amine (TPA)

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During the last 15 years many complexing agents for alkali-metal ions have been synthesized and studied.[2] It seems to be accepted that an efficient replacement of bound water molecules by alkali-metal ions can only be achieved with ligands that offer an optimal distribution of hard donor atoms around the central cation.

High stabilities and high selectivities have been obtained by the use of macrocyclic polyethers (crown ethers, **1**) (Figure 1) and polycyclic polyethers (cryptates, **2**). In both cases the high stability is ascribed to the high structural organization of the ligands. Holes of the right dimension to fit a specific alkali-metal ion are assumed to be preformed in the ligands.[2]

Vögtle has shown that open-chain polypodal compounds based on glyme polyethers can form stable complexes with alkali-metal and alkaline-earth-metal ions[3] (open-chain cryptates).

In the present paper it is shown that alkali-metal complexes with high stability can also be formed with polypodal ligands **3** (Figure 1) without glyme ether functions. In this case a cavity of the right dimension seems to be formed from the assembly of two bowl-shaped hemispheres.

In an investigation of the quadridentate ligand tris(2-pyridylmethyl)amine (tpa) it was discovered that this ligand forms very stable complexes with sodium and potassium.

It is suggested that the structures of these complexes are similar to those of the sodium complexes of the macrobicyclic polypyridine cryptate ligands recently reported by Lehn.[3,4]

The ligand tpa was first described by Anderegg et al.,[5,6] who showed that it forms surprisingly stable 1:1 metal complexes with most of the divalent metal ions in the first transition series.[6]

Tris(2-pyridylmethyl)amine is a symmetric quadridentate ligand of the same general type as tris(2-aminoethyl)amine (tren). In the $[Cu(tpa)Cl]PF_6$ complex tpa ligands were coordinated in a symmetric fashion with the amine nitrogen and the chloride ion situated at the molecular 3-fold axis[7] of a *pseudo* trigonal bipyramid. On the other hand, if tpa is coordinated to a metal(II) ion in order to form a *pseudo*octahedral complex, two adjacent

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