Ion Pairs between Maleonitriledithiolato Complex Dianions of Cobalt and Nickel and Macrocyclic Ligand Complex Dications of Nickel(II) — Control of Intrapair Interaction through Ligand Modification

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The ion pairs $\{[Ni(cyclam)]^{2+}[M(mnt)_2]^{2-}\}$ (M = Co, Ni: **1a,b**), $\{[Ni(tmc)]^{2+}[M(mnt)_2]^{2-}\}$ (M = Co, Ni: **2a,b**) and the solvent complexes $\{[Ni(cyclam)(dmso)_2]^{2+}[M(mnt)_2]^{2-}\}$ (M = Co, Ni, mnt^{2-} = maleonitriledithiolato = (*Z*)1,2-dicyano-1,2-ethylenedithiolato, cyclam = 1,4,8,11-tetraazacyclotetradecane, tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were isolated and structurally characterised. The nature of the macrocyclic ligand and the presence of coordinating solvents determine whether the dication is present as a tetra-, penta- or hexacoordinated complex. In **1a** the tetracoordinated dications and dianions are arranged in a mixed stack structure; the absences of any short contacts and of a mutual ion pair charge transfer band indicate the absence of charge transfer interaction. The highly puckered cyclam ligand will prevent a close approach of the planar bis(maleonitriledithiolato)cobaltate(II). When cyclam is replaced by its tetramethyl derivative tmc, a strong coordinative interaction is introduced as indicated by the structure of **2a**. One dianion coordinates to two dications through two trans-cyano groups. The resulting trinuclear dications $\{[Ni(tmc)][Co(mnt)_2][Ni(tmc)]\}^{2+}$ form segregated columns separated by the non-interacting, remaining dianion. Crystallisation in the presence of a coordinating solvent like dimethyl sulfoxide (dmso) leads to the ion pairs $\{[Ni(cyclam)(dmso)_2]^{2+}[M(mnt)_2]^{2-}\}$containing hexacoordinated dications. Magnetic susceptibility measurements at room temperature are in accord with the observed structures. While **1b** is diamagnetic, **1a**, **2a**, **2b**, and the two solvent complexes exhibit values characteristic of the isolated ions, in agreement with the absence of any electronic interaction between dication and dianion within the ion pair. Temperature- dependent measurements down to 1.7 K indicate that a weak antiferromagnetic interaction is present in **2a**.

Dithiolato metal complexes first gained attention as structural models for the active site of metalloenzymes and metalloproteins.[1] The interest in metal dithiolato compounds revived within the last decade, following the discoveries of unusual physical properties of some of these compounds in the solid state. Research into bis[(*Z*)1,2-ethylenedithiolato] transition metal complexes proved to be most fruitful, affording several compounds with qualities desirable for technical applications, such as conductivity,[2] superconductivity,[3] ferromagnetism[4,5] and photoinduced electron transfer.[6,7] The planar structure of these complexes facilitates formation of stacks, along which long-range interactions can spread. Combined with other planar molecules, they arrange either in segregated[4,8] or mixed stacks.[6,9–12] The low dimensional structure of such compounds often results in anisotropic physical properties, and makes them convenient model systems for studying cooperative phenomena in molecular solids.[2,4,12,13] Bis[(*Z*)1,2-dicyano-1,2-ethylenedithiolato] complexes, which we deal with in this work, have the additional advantage that four cyano groups are available for coordination, which adds to the variety of potential bonding modes. Several ion pairs derived from such [(*Z*)1,2-dicyano-1,2-ethylenedithiolato]metalates were studied in our groups, mainly charge-transfer complexes with organic acceptors. These exhibit interesting electrical[6,14] and optical[9–11,15,16] properties. Recently we reported on the magnetic properties of ion pairs between $[Co(mnt)_2]^{2-}$ (mnt^{2-} = (*Z*)1,2-dicyano-1,2-ethylenedithiolato) and the macrocyclic complexes $[M(tim)]^{2+}$ (M = Ni, or Cu, tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene).[12] $\{[M(tim)]^{2+}[Co(mnt)_2]^{2-}\}$, M = Ni (**NiCo**), Cu (**CuCo**), have isomorphous crystal structures exhibiting a chainlike arrangement of alternating donor and acceptor components. A weak *intrapair* electronic interaction was indicated by the presence of an ion pair charge-transfer absorption band at 850 nm (**NiCo**) or 650 nm (**CuCo**) and by a short interionic contact of 3.15 Å and 3.03 Å between the sulfur atom of the donor and the metal atom of the acceptor in **NiCo** and **CuCo**, respectively. From the magnetic properties of the powder samples in the temperature range of 2 K to 300 K one can conclude that in **NiCo** the diamagnetic $[Ni(tim)]^{2+}$ acceptor allows an efficient pathway for an antiferromagnetic coupling of the spin a half (S = 1/2) ion $[Co(mnt)_2]^{2-}$ along the *a*-axis over a distance of 6.3 Å. The interaction parameter was estimated to $J = -37$ cm^{-1} giving a Weiss temperature of

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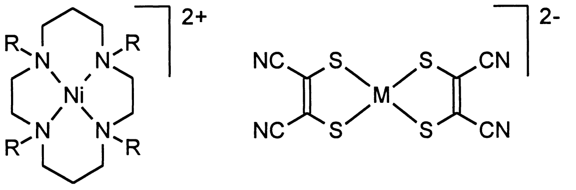
26 K. By contrast, the magnetic orbitals of $[Cu(tim)]^{2+}$ and $[Co(mnt)_2]^{2-}$ remain uncoupled in **CuCo**. Now we extend this study to non-rigid, saturated macrocycle complexes of nickel(II): $[Ni(cyclam)]^{2+}$ and $[Ni(tmc)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane, tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The aim of this work was to examine how the slight variation introduced by employing the alkylated cyclam ligand may influence mutual electronic and magnetic interactions between the ion pair components (Scheme 1).



R = H: **1a**,**b** (M = Co, Ni); R = CH_3: **2a**,**b** (M = Co, Ni)

Scheme 1.

The flexible cyclam ligand can adopt several different arrangements around a central metal atom. A folded *cis* configuration is usually enforced by the presence of a bidentate ligand.[17] For cyclam complexes of nickel, planar *trans* configurations are more common. Four chiral nitrogen atoms give the possibility of five *trans* isomers: *RSRS* (*trans*-I), *RSRR* (*trans*-II), *RRSS* (*trans*-III), *RSSR* (*trans*-IV) and *RRRR* (*trans*-V). The lowest-energy *trans*-III form[18] is usually found in cyclam complexes.[17,19–23] It is postulated that this most stable configuration is acquired via interconversion from the initially formed *trans*-I configuration — the process, which includes dissociation of NH protons.[24] If hydrogen atoms are replaced with methyl groups, such interconversion is not possible, and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane reacts with Ni^{2+} to give relatively stable *trans*-I $[Ni(tim)]^{2+}$,[20,25] which interconverts to *trans*-III only in strongly coordinating solvents.[26] The square planar $[Ni(cyclam)]^{2+}$ complex, with free axial coordination sites forms both stacked and polymeric structures, and several of its compounds exhibit magnetic properties at low temperatures.[21,27]

Results and Discussion

When equimolar solutions of $(TBA)_2[M(mnt)_2]$ (TBA = tetrabutylammonium) in acetone and of $[Ni(cyclam)](ClO_4)_2$ in methanol were mixed, $[Ni(cyclam)][Co(mnt)_2]$ (**1a**) and $[Ni(cyclam)][Ni(mnt)_2]$ (**1b**) precipitated immediately in the form of dark brown and brick-red powders, respectively. $[Ni(tmc)][Co(mnt)_2]$ (**2a**) and $[Ni(tmc)][Ni(mnt)_2]$ (**2b**) were synthesised similarly; in this case, precipitation occurred not immediately but within two hours, affording black crystals. Crystals of **1a**, suitable for X-ray analysis, were obtained by slow diffusion of an acetone solution of $(TBA)_2[Co(mnt)_2]$ into a methanol–dmso (10/1, v/v) solution of $[Ni(cyclam)](ClO_4)_2$. **1a•2dmso** and **1b•2dmso** were obtained by recrystallisation of **1a** and **1b** from saturated dmso solutions. The colours of the two solvated salts do not differ from those of solvent-free **1a** and **1b**. All compounds are soluble in dmso and dmf and insoluble in other common organic solvents and water. Cobalt-containing salts are slightly air-sensitive due to the low oxidation potential of $[Co(mnt)_2]^{2-}$ anion.

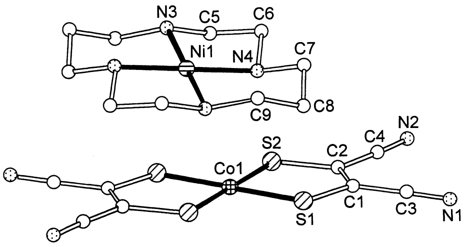


Fig. 1. Structure of $[Ni(cyclam)][Co(mnt)_2]$ (**1a**).

Table 1. Selected Bond Lengths (Å) and Angles (°) for $[Ni(cyclam)][Co(mnt)_2]$ (**1a**)

Ni1–N3	1.945(4)	C1–C2	1.364(7)
Ni1–N4	1.943(4)	C1–C3	1.431(7)
Co1–S1	2.169(2)	C2–C4	1.426(7)
Co1–S2	2.174(2)	C3–N1	1.134(7)
S1–C1	1.734(5)	C4–N2	1.149(7)
S2–C2	1.732(5)		
N3–Ni1–N4	93.3(2)	S1–C1–C3	118.4(4)
S1–Co1–S2	91.9(1)	S2–C2–C4	117.8(4)
Co1–S1–C1	103.6(2)	C1–C2–C4	121.7(5)
Co1–S2–C2	103.6(2)	C2–C1–C3	121.2(4)
S1–C1–C2	120.4(4)	C1–C3–N1	179.0(6)
S2–C2–C1	120.5(4)	C2–C4–N2	178.2(5)

1a crystallises in the triclinic system, space group $P\bar{1}$. The four nitrogen atoms of the cyclam ligand and the central nickel atom form a square planar geometry (Fig. 1, Table 1), with a maximum deviation from the mean plane of 0.561 Å for C8. The average Ni–N bond length of 1.944 Å is characteristic for $[Ni(cyclam)]^{2+}$ in a low-spin state.[20] The complex adopts the expected *trans*-III configuration, with the two six-membered C_3N_2Ni rings in chair conformations; the two hydrogen atoms at the nitrogen atoms of one ring are in *cis*-position relative to each other, but in *trans*-position with respect to their counterparts at the other ring. $[Co(mnt)_2]^{2-}$ has a planar structure, in good agreement with literature data.[28] All metal atoms occupy centres of inversion. Therefore, the distance between Co atoms corresponds to the lattice constants and the distance between Ni and Co is equal to $c/2$. Anion and cation are arranged face-to-face, forming a mixed-stacked structure along the c axis. The angle between the planes of the two complex ions, defined by Ni–N3–N4 and Co–S1–S2, is 16.2°, which places **1a** between the coplanar (5°) and non-coplanar (30°) structures of methyl viologen-dithiolene metalates[9,10] and $[M(tim)][Co(mnt)_2]$,[12] respectively. The closest intra-stack distance of 3.814 Å is found between Ni and S2.

The compounds **1a•2dmso** and **1b•2dmso** are isomorphic; they crystallise in the triclinic system, space group $P\bar{1}$. Similarities and differences between the structures of the unsolvated and solvated complexes are discussed for the case of **1b•2dmso** (Table 2). Similarly to the solvent-free **1a**, the *trans*-III configuration is also present in both solvated com-

Table 2. Selected Bond Lengths (Å) and Angles (°) for $[Ni(cyclam)(dmso)_2][Ni(mnt)_2]$ (**1b·2dmso**)

Ni1–N1	2.040(4)	S2–C21	1.726(4)
Ni1–N2	2.048(4)	S3–C31	1.729(4)
Ni1–O1	2.156(3)	C21–C31	1.354(6)
O1–S1	1.500(3)	C21–C22	1.419(6)
Ni2–S2	2.152(2)	C31–C32	1.414(6)
Ni2–S3	2.145(2)	N21–C22	1.139(6)
		N31–C32	1.146(6)
N1–Ni1–N2′[a]	94.2(2)	S2–C21–C31′	120.5(3)
N1–Ni1–O1	91.4(1)	S3–C31–C21′	120.2(3)
N2–Ni1–O1	96.3(1)	S2–C21–C22	117.6(3)
Ni1–O1–S1	148.8(2)	S3–C31–C32	117.1(3)
S2–Ni2–S3′	92.4(1)	C21′–C31–C32	122.7(4)
Ni2–S2–C21	103.3(2)	C31′–C21–C22	121.9(4)
Ni2–S3–C31	103.6(2)	C21–C22–N21	178.7(5)
		C31–C32–N31	178.1(5)

a) $-x + 1, -y, -z$

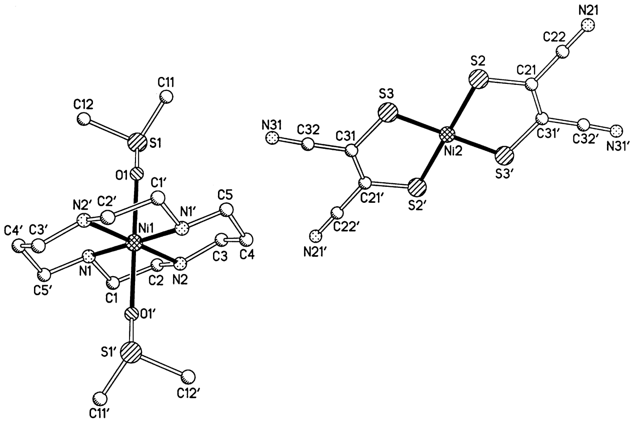


Fig. 2. Structure of $[Ni(cyclam)(dmso)_2][Ni(mnt)_2]$ (**1b·2dmso**).

pounds. The two dmso molecules coordinate to nickel in axial positions via oxygen atoms, resulting in an elongated octahedron structure (Fig. 2). The average Ni–N bond length of 2.044 Å is about 0.1 Å longer than in **1a**, but similar to the lengths in *trans*-coordinated, high-spin nickel(II) cyclam complexes.[21–23] Ni–O bond lengths (2.156 Å) fall within the values found in corresponding compounds.[29] All metal atoms occupy centres of inversion. The ions form segregated stacks along the (100) direction (Fig. 3). The planar $[M(mnt)_2]^{2-}$ ions are almost perpendicular to the stacking direction.

2a crystallises in the monoclinic system, space group $P2_1/c$. Contrary to the structure of the cyclam complexes, the tmc ligand induces a *RSRS* (*trans*-I) configuration (Fig. 4, Table 3), with all four methyl groups in *cis*-positions, i.e. on one side of the NiN_4 plane. On the same side, one CN group of the mnt-ligand of the bis(maleonitrileditiolato)cobaltate(II) coordinates to nickel through the N8 atom, resulting in a pentacoordinated complex. The average distance between the nitrogen atoms of the tmc ligand and nickel is found to be 2.120 Å, a typical value for pentacoordinated high-spin $[Ni(tmc)L]^{2+}$ complexes.[30–32] This is longer by 0.14 Å than the distance for square-planar, low-spin $[Ni(tmc)]^{2+}$.[25,33] The bond between Ni and the nitrogen atom of the CN group is 1.994 Å, shorter by about 0.13 Å than the distances to nitrogen atoms of tmc, and similar to the bond lengths of 1.95 and 1.98 Å reported for $[Ni(tmc)(N_3)]^{+}$ [30] and $[Ni(tmc)(CH_3CN)]^{2+}$,[32] respectively. The geometry of the nickel complex **2a** is intermediate between a square pyramid and a trigonal bipyramid. For the tmc nitrogen atoms N1 and N3, ascribed to axial positions in the trigonal bipyramid approximation, an N1NiN3 angle of 172.0° is observed, whereas for the equatorial N2 and N4 atoms the corresponding angle N2NiN4 is equal to 153.5°. The coordination geometry around Ni differs significantly from square-pyramidal complexes like $[Ni(tmc)(N_3)]^{2+}$, [30] $[Ni(tmc)(CH_3CN)]^{2+}$ [32] and $[Ni(tmc)(C_6H_5S)]^{+}$.[34] The closest related structure is that of $[Ni(tmc)(dmf)]^{2+}$ (dmf = *N*,*N*-dimethylformamide).[32] The parameters of the planar $[Co(mnt)_2]^{2-}$ again correspond to literature data.[28] One of the dianions (Co2) is coordinated to two

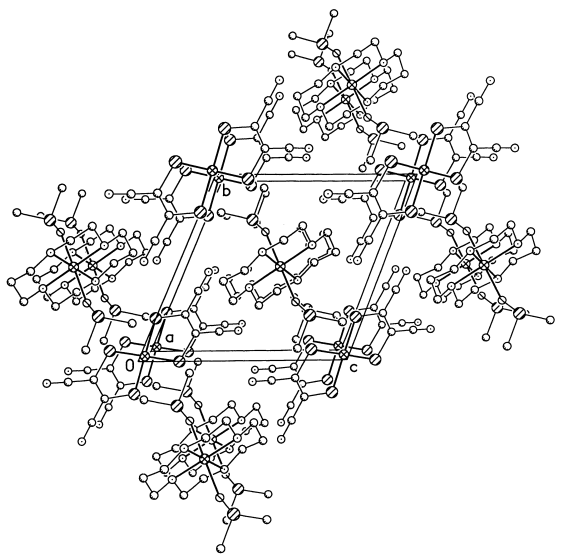


Fig. 3. Packing diagram of $[Ni(cyclam)(dmso)_2][Ni(mnt)_2]$ (**1b·2dmso**) along the *a* axis.

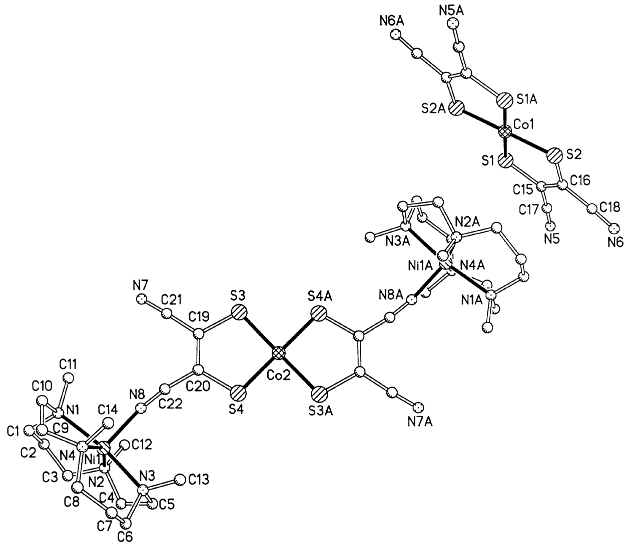


Fig. 4. Structure of $[Ni(tmc)][Co(mnt)_2]$ (**2a**).

Table 3. Selected Bond Lengths (Å) and Angles (°) for [Ni(tmc)][Co(mnt)$_2$] (**2a**)

Ni1–N1	2.131(7)	S3–C19	1.736(9)
Ni1–N2	2.091(8)	S4–C20	1.729(9)
Ni1–N3	2.137(7)	C15–C16	1.34(1)
Ni1–N4	2.121(7)	C15–C17	1.43(1)
Ni1–N8	1.994(7)	C16–C18	1.47(1)
Co1–S1	2.175(3)	C19–C20	1.39(1)
Co1–S2	2.176(3)	C19–C21	1.43(1)
Co2–S3	2.179(3)	C20–C22	1.41(1)
Co2–S4	2.162(2)	C17–N5	1.16(1)
S1–C15	1.751(9)	C18–N6	1.13(1)
S2–C16	1.73(1)	C21–N7	1.13(1)
		C22–N8	1.13(1)
N1–Ni1–N2	93.1(3)	S1–C15–C16	119.7(8)
N1–Ni1–N3	172.0(3)	S2–C16–C15	122.1(8)
N1–Ni1–N4	84.3(3)	S3–C19–C20	119.0(7)
N1–Ni1–N8	94.5(3)	S4–C20–C19	120.8(8)
N2–Ni1–N3	85.4(3)	S1–C15–C17	116.3(7)
N2–Ni1–N4	153.5(4)	S2–C16–C18	118.1(7)
N2–Ni1–N8	101.3(3)	S3–C19–C21	117.1(7)
N3–Ni1–N4	93.5(3)	S4–C20–C22	117.7(8)
N3–Ni1–N8	93.5(3)	C15–C16–C18	120(1)
N4–Ni1–N8	105.2(3)	C16–C15–C17	123.9(9)
S1–Co1–S2	91.8(1)	C19–C20–C22	121.4(9)
S3–Co2–S4	91.7(1)	C20–C19–C21	123.8(9)
Ni1–N8–C22	172.0(8)	C15–C17–N5	178(1)
Co1–S1–C15	103.3(3)	C16–C18–N6	176(1)
Co1–S2–C16	102.9(3)	C19–C21–N7	178(1)
Co2–S3–C19	104.3(3)	C20–C22–N8	171(1)
Co2–S4–C20	104.1(4)		

cations through the *trans* cyano groups of two mnt ligands, forming a Ni–Co–Ni trimer structure with the Co2 anion in a position almost perpendicular to the NiN4 planes (Fig. 4). The trinuclear dications are located across the cell (Fig. 5), forming columns along the (010) direction. The second, uncoordinated dianion (Co1) is placed between neighbouring trimers in the column, parallel to the bases of the square pyramidal [Ni(tmc)]$^{2+}$ components. All cobalt atoms occupy centres of inversion.

Electronic Spectra. The UV-vis-NIR diffuse reflectance spectra of **1a** and **1b** correspond to those of (TBA)$_2$[Co(mnt)$_2$][12,16] and (TBA)$_2$[Ni(mnt)$_2$],[14] respectively. Weak d–d bands of the [Ni(cyclam)]$^{2+}$ ion are covered by high intensity metal-to-ligand charge-transfer bands of [Co(mnt)$_2$]$^{2-}$. In the spectra of **2a** and **2b** (Fig. 6) new bands at 1500 nm and shoulders around 800 (**2a**) and 700 nm (**2b**) appear. These are absent in the simple [(*Z*),2-dicyano-1,2-ethylenedithiolato]metalates. They are characteristic for d–d transitions of Ni(II) surrounded by five ligands, as also reported for other [Ni(tmc)L]$^{2+}$ complexes: L = Cl$^-$, Br$^-$, NCS$^-$ [35] and O$_2$-COCH$_3$.[31]

Magnetic Properties. Magnetic susceptibility measurements were performed at room temperature on a magnetic balance. **1a** exhibits a magnetic moment of $\chi_m T = 0.63$ cm^3 mol^{-1} K, which corresponds to the spin of one unpaired electron at Co(II). From this, a value of $g_{Co} = 2.59$ is calculated which is typical for cobalt in a strong, square-planar ligand field.[12] Ni(II) in a square-planar complex is expected to be in a low-spin state and therefore not to contribute to the magnetic moment. Accordingly, **1b**, which is composed of two planar nickel complexes was found to be diamagnetic. But the solvated complex **1b·2dmso** exhibits a $\chi_m T$ value of 1.10 cm^3 mol^{-1} K,

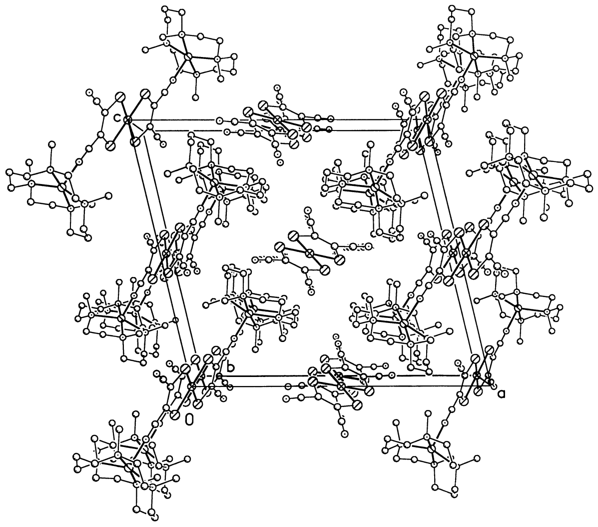


Fig. 5. Packing diagram of [Ni(tmc)][Co(mnt)$_2$] (**2a**) along the *b* axis.

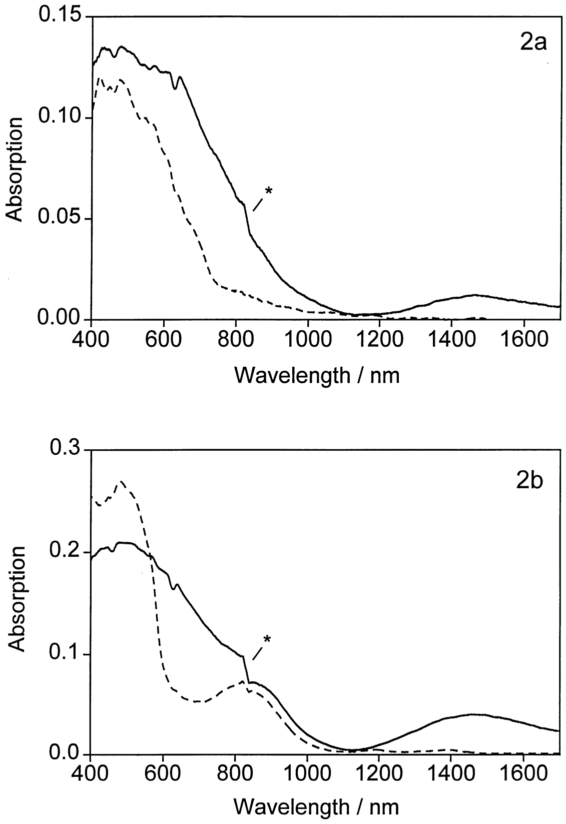


Fig. 6. Diffuse reflectance spectra of [Ni(tmc)][Co(mnt)$_2$] (**2a**) and [Ni(tmc)][Ni(mnt)$_2$] (**2b**) (solid lines) in comparison to the spectra of (TBA)$_2$[Co(mnt)$_2$] and (TBA)$_2$-[Ni(mnt)$_2$] (broken lines), respectively. *Technical artifact.

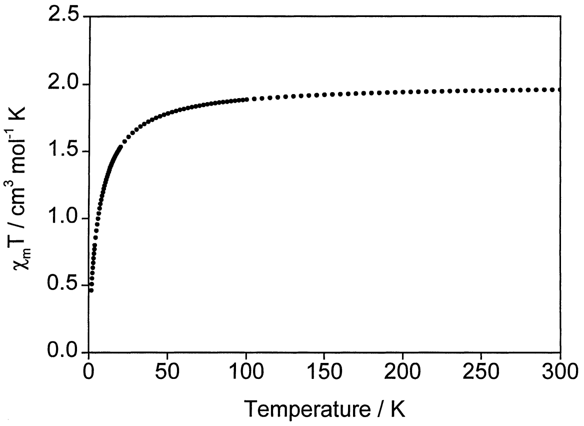


Fig. 7. Temperature dependence of $\chi_m T$ for [Ni(tmc)]-[Co(mnt)$_2$] (**2a**) at applied field of 0.1 T.

which indicates that high-spin (S = 1) Ni(II) is in an octahedral environment. The calculated g_{Ni} value of 2.10 is characteristic for *trans*-[Ni(cyclam)L$_2$]$^{2+}$ complexes, L = Cl$^-$, Br$^-$ [19,22] and CrO$_4{}^{2-}$.[21]

2a and **2b** exhibit $\chi_m T$ values of 1.97 and 1.31 cm^3 mol^{-1} K, respectively, which are consistent with S = 1 + 1/2 and S = 1 systems and corroborate the presence of a distorted square-pyramidal geometry, which is required for Ni(II) in a high-spin configuration. Taking g_{Co} = 2.59, as calculated for **1a**, g_{Ni} values of 2.32 (**2a**) and 2.29 (**2b**) are obtained, which match the values found for other pentacoordinated tmc complexes of Ni(II).[35] For complex **2a** the temperature dependence of the susceptibility was measured with a SQUID magnetometer down to 1.7 K. The magnetic dc susceptibility of **2a** exhibits a weak antiferromagnetic interaction and obeys the Curie–Weiss law with C = 1.97 cm^3 mol^{-1} K and Θ = 6.20 K. $\chi_m T$ decreases monotonously upon cooling. At 300 K $\chi_m T$ = 1.97 cm^3 mol^{-1} K is identical with C within the experimental error (Fig. 7).

Conclusions

The combination of [M(mnt)$_2$]$^{2-}$, M = Co, Ni, with [Ni(cyclam)]$^{2+}$ and [Ni(tmc)]$^{2+}$ affords the ion pairs {[NiL]$^{2+}$ [M(mnt)$_2$]$^{2-}$}, the structure of which is determined by the nature of the macrocyclic ligand and the presence of coordinating solvents. {[Ni(cyclam)]$^{2+}$ [Co(mnt)$_2$]$^{2-}$} (**1a**) forms a stacked structure of alternating ions. However, the distance between neighbouring nickel and sulfur atoms is significantly longer than the sum of van der Waals radii and no mutual charge-transfer interaction can be detected by electronic absorption spectroscopy. Most likely the highly puckered cyclam ligand prevents a close approach of the planar counter ion such as is possible in the case of the flat [M(tim)]$^{2+}$ complexes.[12] In agreement with the absence of any interaction between the two ion pair components, Ni(II) in **1a** remains in low-spin state characteristic for a square-planar structure. The solvated complex **1a·2dmso** contains the octahedrally coordinated [Ni(cyclam)(dmso)$_2$]$^{2+}$ ion. Accordingly, Ni(II) adopts a high-spin configuration (S = 1). In {[Ni(tmc)]$^{2+}$ [Co(mnt)$_2$]$^{2-}$} (**2a**), the presence of the tmc ligand induces a strong bonding interaction between the two ion pair components through coordination of two CN groups of one [Co(mnt)$_2$]$^{2-}$ component at two neighbouring [Ni(tmc)]$^{2+}$ ions. As a result a trinuclear dication is obtained, the charge of which is neutralised by another dianion, lacking any interaction. The latter may be responsible for the absence of any long-range magnetic coupling. In agreement with a distorted square-pyramidal coordination, Ni(II) is in a high-spin state and new d–d absorption bands appear in the diffuse reflectance electronic spectra.

Experimental

Materials. [Ni(cyclam)](ClO$_4$)$_2$,[19] [Ni(tmc)](ClO$_4$)$_2$,[35] (TBA)$_2$-[Co(mnt)$_2$] and (TBA)$_2$[Ni(mnt)$_2$][36] complexes were prepared by methods described in the literature. Other reagents and solvents of analytical grade were used as supplied. All syntheses and measurements for compounds containing [Co(mnt)$_2$]$^{2-}$ were performed under nitrogen using standard Schlenk techniques.

Syntheses. [Ni(cyclam)][Co(mnt)$_2$] (1a): A methanolic solution (80 mL) of [Ni(cyclam)](ClO$_4$)$_2$ (0.5 mmol, 0.23 g) was added to an acetone solution (30 mL) of (TBA)$_2$[Co(mnt)$_2$] (0.5 mmol, 0.41 g). The resulting precipitate was filtered off, washed with MeOH–acetone (2:1, v/v), then with acetone and dried in vacuo. Dark brown powder (0.14 g, 47%). Found: C, 36.48; H, 4.19; N, 18.75%. Calcd for $C_{18}H_{24}N_8S_4NiCo$: C, 36.14; H, 4.04; N, 18.73%. Crystals of **1a** were obtained by slow diffusion of a MeOH–acetone–dmso (10:10:1, v/v/v) solution of [Ni(cyclam)]-(ClO$_4$)$_2$ into an acetone solution of (TBA)$_2$[Co(mnt)$_2$].

[Ni(cyclam)][Ni(mnt)$_2$] (1b) was prepared analogous to **1a** using (TBA)$_2$[Ni(mnt)$_2$] (0.5 mmol, 0.41 g). Brick-red powder (0.15 g, 50%). Found: C, 36.51; H, 4.25; N, 18.77%. Calcd for $C_{18}H_{24}N_8S_4Ni_2$: C, 36.15; H, 4.04; N, 18.74%.

1a·2dmso and **1b·2dmso** were obtained by recrystallisation of 1a and 1b, respectively, from saturated dmso solution.

[Ni(tmc)][Co(mnt)$_2$] (2a): A solution of [Ni(tmc)](ClO$_4$)$_2$ (0.5 mmol, 0.26 g) in acetone–MeOH (4:1, v/v, 100 mL) was added to an acetone solution (40 mL) of (TBA)$_2$[Co(mnt)$_2$] (0.5 mmol, 0.41 g). After 4 h half of the solvent was removed by slow evaporation at room temperature and the mixture was allowed to stand for two days. The resulting crystalline product was filtered off, washed several times with acetone and dried in vacuo. Dark brown crystals (0.20 g, 61%). Found: C, 40.33; H, 4.97; N, 17.15%. Calcd for $C_{22}H_{32}N_8S_4Ni_2$: C, 40.38; H, 4.93; N, 17.12%.

[Ni(tmc)][Ni(mnt)$_2$] (2b) was prepared analogous to **2a** using (TBA)$_2$[Ni(mnt)$_2$] (0.5 mmol, 0.41 g). Dark brown crystals (0.17 g, 52%). Found: C, 40.42; H, 5.06; N, 17.04%. Calcd for $C_{22}H_{32}N_8S_4Ni_2$: C, 40.39; H, 4.93; N, 17.13%.

Analytical Methods and Physical Measurements. Carbon, nitrogen and hydrogen were determined by micro analysis on a Carlo Erba Elemental Analyser 1106. Infrared spectra and UV-vis-NIR diffuse reflectance spectra (relative to alumina) were recorded from nujol mulls on a Perkin Elmer 16PC FT-IR spectrometer and on a Shimadzu UV 3101 PC spectrometer, respectively. Magnetic susceptibility at room temperature was measured on a Johnson Matthey magnetic susceptibility balance. The temperature dependence of the magnetic susceptibility of a powdered sample **1a** was measured with a Quantum Design MPMS2 SQUID magnetometer in the temperature range 1.7 to 300 K with an applied field of 0.1 T. Experimental susceptibility data were corrected for diamagnetism using Pascal's constants.[37]

X-ray Structural Determinations. Crystals were sealed in glass capillaries under argon or nitrogen. Measurements were performed on a Mac Science MXC3KHF four-circle automated diffractometer (**1a**), an Enraf-Nonius CAD4 (**1a·2dmso**) and a Si-

Table 4. Crystal Data and Refinement Details for [Ni(cyclam)][Co(mnt)$_2$] (**1a**), [Ni(cyclam)(dmso)$_2$][Co(mnt)$_2$] (**1a•2dmso**), [Ni(cyclam)(dmso)$_2$][Ni(mnt)$_2$] (**1b•2dmso**) and [Ni(tmc)][Co(mnt)$_2$] (**2a**)

Compound	**1a**	**1a•2dmso**	**1b•2dmso**	**2a**
Formula	$C_{18}H_{24}CoN_8NiS_4$	$C_{22}H_{36}CoN_8O_2NiS_6$	$C_{22}H_{36}N_8Ni_2O_2S_6$	$C_{22}H_{32}CoN_8NiS_4$
Formula weight	589.33	754.57	754.37	654.44
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group (No.)	$P\bar{1}$(2)	$P\bar{1}$(2)	$P\bar{1}$(2)	$P2_1$/c(14)
a / Å	8.952(16)	8.766(5)	8.183(4)	18.623(8)
b / Å	9.699(19)	10.553(6)	10.526(5)	9.395(3)
c / Å	8.550(11)	10.261(6)	10.550(6)	17.233(7)
α / °	110.78(13)	68.01(4)	68.26(3)	90.0
β / °	112.62(13)	86.11(5)	85.99(4)	103.82(4)
γ / °	66.00(14)	74.53(5)	75.12(4)	90.0
V /Å^3	608.5(2)	841.52(9)	815.5(7)	2928(2)
Z	1	1	1	4
D_c /g cm^{-3}	1.632	1.49	1.536	1.485
Crystal size / mm	0.70 × 0.30 × 0.20	0.36 × 0.31 × 0.22	0.50 × 0.40 × 0.10	0.50 × 0.28 × 0.05
Temperature / K	295	294	200	298
λ (Mo $K\alpha$)/Å	0.71073	0.71073	0.71073	0.71073
F (000)	306	391	392	1356
μ/cm^{-1}	18.12	14.56	15.73	15.22
$2\theta_{max}$ /°	55.0	55.0	54.1	52.0
Reflections measured	3080	4059	3626	6846
Reflections used	1743	2351	3503	5541
No. of parameters	196	257	256	332
Correction made	psi-scan	psi-scan	none	psi-scan
Final R	0.028	0.040	0.0468	0.0657
Final wR_2 $^{a)}$ or R_w $^{b)}$	0.041	0.059	0.1129	0.1263
Goodness of fit	2.01	1.16	1.072	1.045
$\Delta\gamma_{max}$ / eÅ^{-3}	0.680	0.562	0.522	0.786

a) wR_2 for **1a** and **1a•2dmso**; b) R_w *for* **1b•2dmso** and **2a**.

emens P4 diffractometer (**1b•2dmso** and **2a**) with graphite-monochromated Mo-$K\alpha$ radiation. Crystal data and experimental details are given in Table 4. Except for **1b•2dmso**, data were corrected for absorption[38] (**1a**, **1a•2dmso** and **2a**). The structures were solved by direct methods and subsequent Fourier-difference techniques, including full-matrix least squares refinement on F^2 (**1b•2dmso** and **2a**) or F (**1a** and **1a•2dmso**).[39] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier synthesis and were refined isotropically (**1a**, **1a•2dmso** and **1b•2dmso**), except for **2a**, in which case they were geometrically positioned.

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