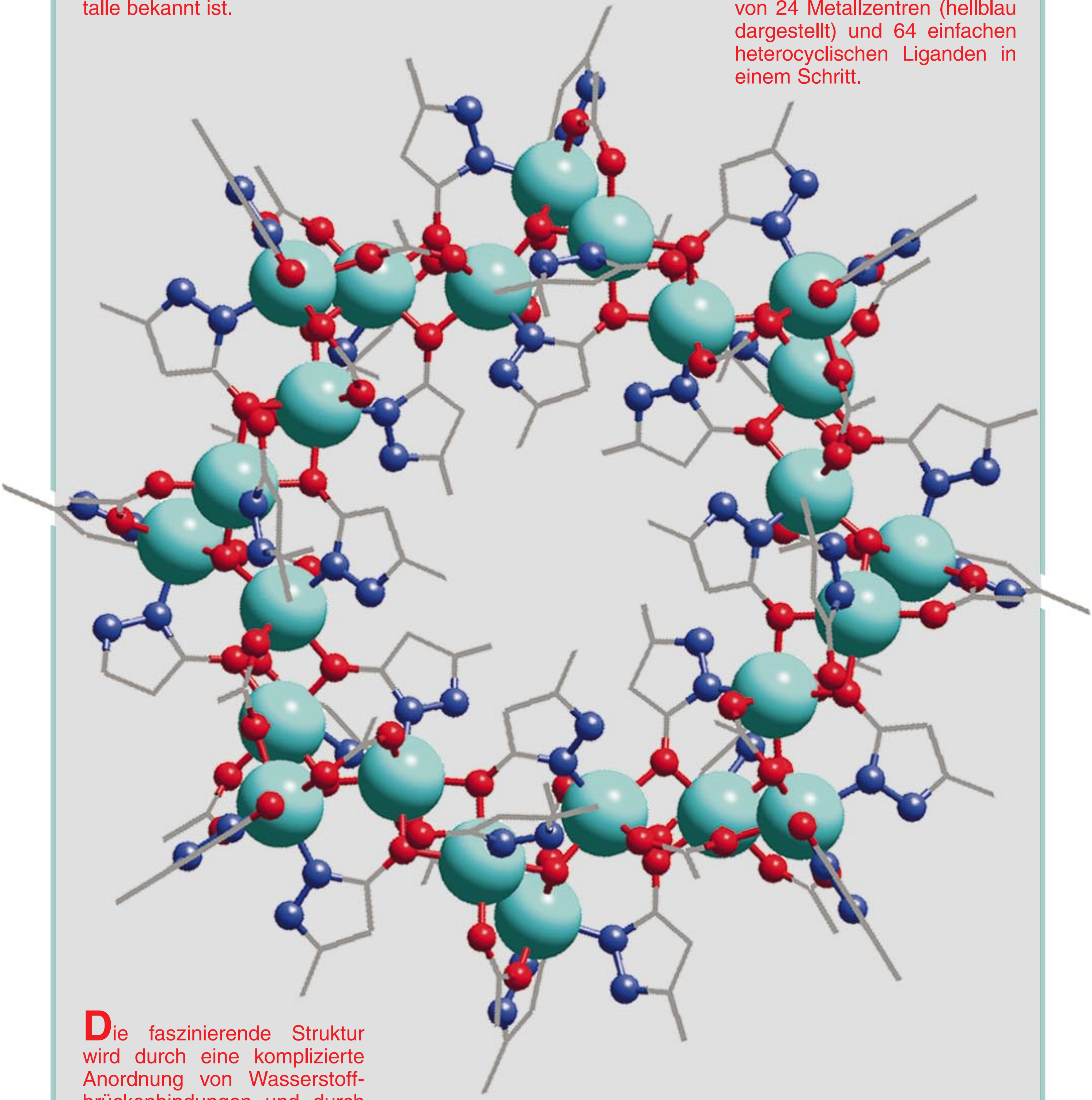
Das abgebildete „Nickelrad“ ist die bisher größte cyclische Käfigstruktur, die für 3d-Metalle bekannt ist.

Aus supramolekularer Sicht ist die Käfigverbindung das Ergebnis der Selbstanordnung von 24 Metallzentren (hellblau dargestellt) und 64 einfachen heterocyclischen Liganden in einem Schritt.



Die faszinierende Struktur wird durch eine komplizierte Anordnung von Wasserstoffbrückenbindungen und durch eine geeignete Orientierung der Methylgruppen innerhalb des makrocyclischen Hohlraumes stabilisiert.

Mehr zu diesem Thema erfahren Sie auf den folgenden Seiten.

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Synthesis, Structure, and Preliminary Magnetic Studies of a Ni_{24} Wheel[**]

Angela L. Dearden, Simon Parsons, and
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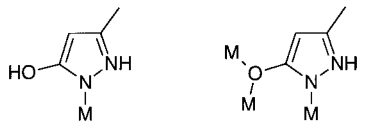
Metal rings have excited mankind since mythological times.[1] The largest cyclic structure containing exclusively paramagnetic 3d-metals is the Fe_{18} wheel reported by Lippard and co-workers,[2] which is an order of magnitude smaller than the giant wheels constructed from molybdate fragments by the Müller group.[3] We have previously reported[4] a Ni_{12} wheel featuring acetate and 6-chloro-2-pyridonate ligands which shows ferromagnetic exchange between the metal centers, and a resulting $S = 12$ spin ground state. Herein we report initial experiments involving the heterocyclic ligand, 3-methyl-3-pyrazolin-5-one (Hmpo) (Scheme 1), which result in the formation of a cyclic Ni_{24} cage.



(a) Hmpo binding mode (b) mpo binding mode

(c) μ_3-O_2CMe (d) μ_2-O_2CMe

Scheme 1.

Hmpo and hydrated nickel acetate were stirred together in MeOH for 24 h, during which time a pale green precipitate formed, which was removed by filtration. The solution was evaporated to dryness, the resulting powder was redissolved in MeCN and green rodlike crystals grew over two days. X-ray analysis[5] (Figure 1) revealed a tetraicosanuclear nickel cage $[Ni_{24}(OH)_8(mpo)_{16}(O_2CMe)_{24}(Hmpo)_{16}]$ (**1**; mpo = the monodeprotonated anion of Hmpo).

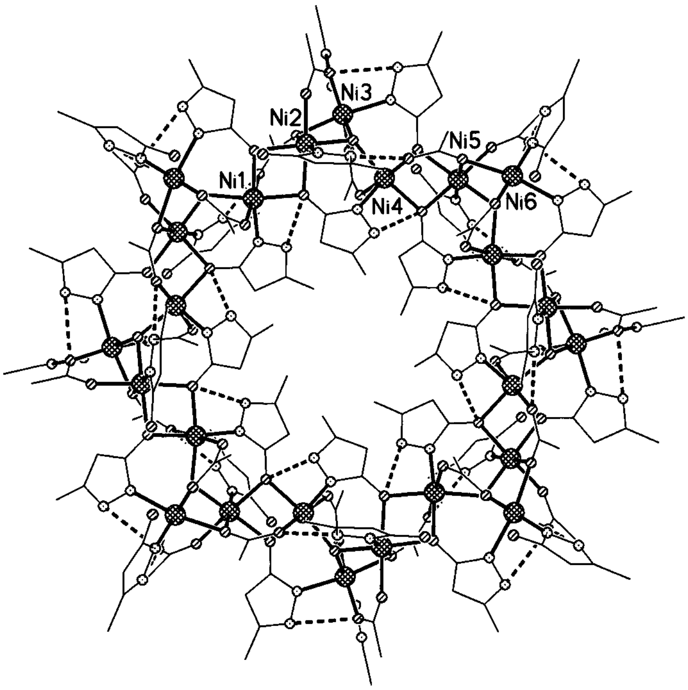


Figure 1. The structure of **1** in the crystal. Hydrogen bonds are shown as dashed lines.

The cage is disposed about a crystallographic fourfold axis therefore there are only six nickel centers in the asymmetric unit. However, in many ways the structure can be described as consisting of an octamer of chemically equivalent trinuclear building blocks. The first such unit contains Ni1, Ni2, and Ni3, while Ni4, Ni5, and Ni6 belong to the second (Figure 2). Thus the structural role and coordination environment of Ni4 is equivalent to Ni1, Ni5 equivalent to Ni2, and Ni6 to Ni3. In the following paragraph only the first trinuclear building block is discussed, with the relevant metal sites in the second fragment identified in parentheses.

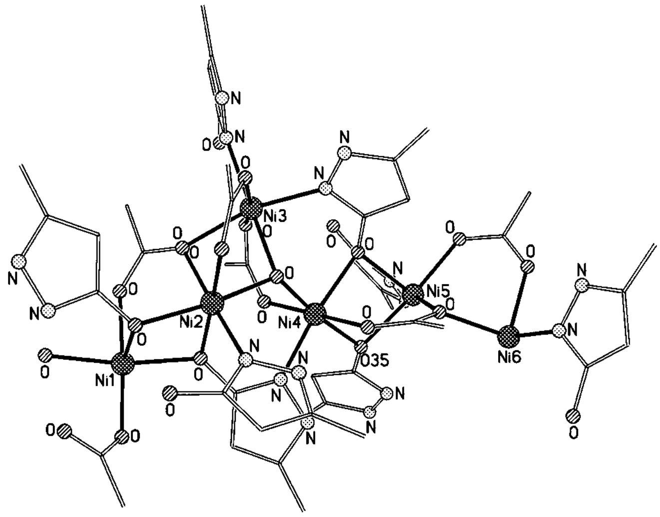


Figure 2. The asymmetric unit of **1**. Bond length ranges [Å]: Ni-O(mpo) 2.055–2.140, Ni-O(acetate) 2.034–2.137, Ni-O(OH) 2.011–2.049, Ni-N(mpo) 2.024–2.060, Ni-N(Hmpo) 2.079–2.096; (average esd 0.003 Å).

The bridging within the blocks is predominantly performed by acetate and mpo ligands (Scheme 1). One acetate bridges in a μ_3-fashion, that is, bridging Ni1 (Ni4) and Ni2 (Ni5) with the oxygen atom bound to Ni2 (Ni5) also bound to Ni3 (Ni6). The two mpo ligands within the trinuclear fragment also

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bridge the Ni1 $\cdots$ Ni2 (Ni4 $\cdots$ Ni5) vector through the exocyclic oxygen atom, with the ring nitrogen atom bound to a nickel center in a neighboring trimer. A second carboxylate group bridges Ni2 (Ni5) and Ni3 (Ni6) in a 1,3-fashion, with a μ_3-hydroxide also bridging this vector and binding on to Ni4 (Ni1) in the next trinuclear fragment. Thus a 1,3-carboxylate group and two μ_2-oxygen atoms bridge each Ni $\cdots$ Ni contact within the building blocks. This means of bridging M $\cdots$ M is found in other cyclic structures such as the Ni_{12} cage we reported,[4] and the decanuclear "ferric wheel" described by Lippard and co-workers.[6] The two neutral Hmpo ligands within each trinuclear block are attached through the ring nitrogen atom to Ni2 (Ni5) and Ni3 (Ni6).

The linking between trinuclear blocks involves a μ_3-hydroxide unit which bridges between Ni2 and Ni3 in one unit and Ni4 in the second, or Ni5, Ni6, and Ni1. The link is further supported by μ_2-carboxylate units which bridge Ni3 $\cdots$ Ni4 and Ni6 $\cdots$ Ni1. Additionally the four mpo ligands each bind to two metal centers from one trinuclear block through the O-donor, while binding to a third metal center from the other fragment through the N-donor, for example, bridging Ni4 and Ni5 in the second block, while the ring nitrogen atom binds to Ni3 in the first.

This complicated set of interactions generates the Ni_{24} structure, which is much less circular than other cyclic structures (Figure 1). The trinuclear fragments are so disposed that they point approximately at the center of the neighboring unit, rather than at the end. The angle between the lines Ni1-Ni2-Ni3 and Ni4-Ni5-Ni6 is 51.0°. This generates a structure where Ni3, Ni6 and their symmetry equivalents create distinct "points" on the wheel. In addition to the metal–ligand bonding described above, the structure is stabilized by a large quantity of H bonding. The majority of these interactions arise from the proton on the second N atom within the pyrazolinone ligands. Thus H bonds are formed between this site and O atoms from both acetate and mpo ligands (Figure 1).

All the metal centers are six-coordinate, with approximately octahedral symmetry. Four of the crystallographically independent sites (Ni1, Ni2, Ni4 and Ni5) are bound to one N- and five O-donor groups, while the remaining two sites (Ni3 and Ni6) have two N- and four O-donor groups. Magnetic measurements[7] are consistent with twenty-four $S = 1$ centers. The room-temperature value for $\chi_m T$ of approximately 30 $cm^3 K mol^{-1}$ (χ_m = molar magnetic susceptibility) matches well with the calculated value ($\chi_m T_{calcd.} = 29\,cm^3 K mol^{-1}$) for a reasonable g-value of 2.2. The $\chi_m T$ declines with temperature, however, even at 1.8 K, $\chi_m T$ is greater than 24 $cm^3 K mol^{-1}$, which indicates that while the magnetic behavior is dominated by antiferromagnetic exchange this is rather weak and many magnetic states remain populated at even very low temperatures. The antiferromagnetic exchange suggests that, in principle, this Ni_{24} cage should be useful for modeling the Haldane gap predicted to occur for wheels or chains of anti-ferromagnetically couple $S = 1$ chains.[8]

It is noticeable that, as with the Fe_{18} structure,[2] it is not possible to generate a large 3d-metal wheel with only one type of bridging interaction. Therefore while decanuclear ferric wheels[6, 9] can be accurately described as $[\{Fe(OMe)_2(O_2CR)\}_{10}]$ (R = Me, CH_2Cl, $CH_2CH_2C(O)C_6H_4Me$), and octanuclear chromium wheels[10] can be described as $[\{CrX(O_2CR)_2\}_8]$ (X = F, R = CMe_3; X = OH, R = Ph) such a description as an oligomer of a mononuclear fragment is not accurate for these larger wheels. For both the Fe_{18} and Ni_{24} wheels a more accurate description is as an oligomer of trinuclear building blocks. Therefore, if still larger wheels are to be constructed, a design principle might be to look for either larger oligomers of trinuclear fragments, or oligomers of higher nuclearity building blocks. This structure using 3-methyl-3-pyrazolin-5-one appears to be the first that involves this ligand; the presence of a suitable H-bond donor within this ligand might also be an important feature in generating this large cage.

The Ni_{24} wheel appears to be the largest homometallic cage containing paramagnetic Ni^{II} centers. Previous examples of cages containing ten or more nickel centers include: $Ni_{16}Na_6$ which contains four Ni_4 cubanes linked by phthalate ligands,[11] the cyclic Ni_{12} wheel mentioned above,[4] a $[Ni_{11}Br_6(N\mathit{t}Bu)_8]$ cage,[12] a series of Ni_{10}, Ni_{11}, and Ni_{12} cages containing a mixture of carboxylate and pyridonate ligands,[13] a dimer of Ni_5 metallocrowns.[14]

Experimental Section

1. A colorless solution of Hmpo (0.02 mol) in MeOH (100 mL) was added to a green solution of hydrated nickel acetate (0.02 mol) in MeOH (100 mL). The resulting green solution was stirred for 24 h at room temperature, during which time a pale green precipitate formed, which was removed by filtration. The solution was evaporated to dryness under reduced pressure and the resulting powder dried in vacuum. This was then redissolved in MeCN to give a saturated solution from which green rodlike crystals grew over two days; yield: 20%, elemental analysis calcd (%) for $C_{67}H_{70}Cl_{14}F_{12}Ni_6O_{20}$: C 35.51, H 3.24, N 6.47; found: C 35.32, H 3.13, N 6.40.

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[5] Crystal data for **1**. $C_{176}H_{256}N_{64}Ni_{24}O_{88} \cdot 15\,C_2H_3N \cdot 6.5\,H_2O$, $M_r = 6760$, tetragonal, $P4/n$ twinned on [110], $a = 37.443(3)$, $c = 12.9254(15)$ Å, $V = 18121(3)$ Å^3, $Z = 2$ (the molecule lies on a fourfold axis), $T = 150.0(2)$ K, crystal size $0.28 \times 0.08 \times 0.08$ mm, $\mu(Mo_{K\alpha}) = 1.289\,mm^{-1}$. Data were collected with a Bruker Smart APEX CCD area detector equipped with an Oxford Cryosystems low-temperature device. An absorption correction was applied based on ψ-scan data (min./max. transmission: 0.708/0.928). The structure was solved by the heavy atom methods ("DIRDIF": P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel, J. M. M. Smits, DIRDIF-96 Program System, University Crystallography Laboratory, University of Nijmegen, The Netherlands **1996**) and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 (G. M. Sheldrick, SHELXL-97, University of Göttingen, **1997**). Hydrogen atoms were included in calculated positions, riding on parent carbon atoms, with $U(H) = 1.2\,U_{eq}(C)$ for aromatic H atoms and $U(H) = 1.5\,U_{eq}(C)$ for methyl hydrogens. There was disorder in the rings of two of the mpo ligands, which was modelled with two half-occupancy geometries. There is also some disordered and part-weight solvent (MeCN and H_2O) in the crystal lattice. All full-weight non-H atoms were refined with

anisotropic displacement parameters: 897 parameters, $wR2 = 0.1835$ for 18516 unique data ($2.69 \le \theta \le 26.39°$), $R1 = 0.0666$ for 14232 data with $F_o > 4\sigma(F)$, max./min. residual electron density 0.789/ −0.549 e Å^3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148156. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Off-the-Shelf Colorimetric Anion Sensors[**]

Hidekazu Miyaji and Jonathan L. Sessler[*]

The recognition[1] and sensing[2] of anionic analytes has emerged recently as a key research theme within the generalized area of supramolecular chemistry.[3] Of particular interest in this regard are "colorimetric anion sensors", species that would allow the so-called "naked-eye" detection of anions without resort to any spectroscopic instrumentation. However, few such systems exist at present.[4–7] For instance, alizarin complexone[4a] has been used to effect the colorimetric sensing of fluoride anions in water, wet acetone, and wet acetonitrile as has 2,3-dipyrrol-2-yl-quinoxaline in dichloromethane.[6b] Thiourea has also been used to sense halide, phosphate, and carboxylate ions.[4b] Appropriately functionalized calix[4]pyrroles also show potential as naked-eye anion sensors.[7] Separately, displacement-based strategies have been used by Lavigne and Anslyn to detect citrate anions colorimetrically[5] and, more recently by Gale et al. to sense halide anions.[6a] Still, there remains a cogent need for species whose changes in color could be used to signal either qualitatively or quantitatively the presence of particular anionic analytes. Such agents would be especially valuable were they to be obtained readily without resort to dedicated synthesis. Herein we report that a wide range of commercially available entities, such as 1,2-diaminoanthraquinone, 1,8-diaminoanthraquinone, 4-nitroaniline, 4-nitro-1,2-phenylenediamine, L-leucine-4-nitroanilide, 1-(4-nitrophenyl)-2-thiourea, 4-nitrophenol, alizarin, 2,2′-bi(3-hydroxy-1,4-naphthoquinone), acid blue 45, naphthol AS, 9(10*H*)-acridone, and Direct Yellow 50 may be used as "off-the-shelf" color-based anion sensors in organic solvent. We also show that some of these agents may be used in combination with a crown ether phase-transfer catalyst to extract and detect anions colorimetrically in a two-phase organic–aqueous set-up, even in those instances where the anions being detected were originally present in the aqueous phase.

Initially, we focused on 1,8-diaminoanthraquinone as a potential off-the-shelf anion sensor. We were attracted to this system because 1) it contains two aniline-like NH_2 donor groups that appeared properly positioned to bind a chloride ion by cooperative hydrogen-bonding interactions, as judged from structural analyses of previous chloride-binding[8] and noncolorimetric sensing agents[2c] containing a similar structural motif, 2) such binding was expected to result in a bathochromic shift in the absorption bands in the visible region,[7b] and 3) various control compounds, with other modifications of the anthraquinone skeleton, would be readily available. In accord with the latter predicative thought, we studied the changes (if any) in the absorption spectra of anthraquinone, 1,2-, 1,4-, 1,5-, 1,8-,[8] and 2,6-diaminoanthraquinone, as well as 1- and 2-aminoanthraquinone, induced upon the addition of various anions, namely F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, and HSO_4^- in dichloromethane. Although, no change in the absorption spectrum of anthraquinone itself was found upon the addition of any of the analytes tested, the spectra of the other anthraquinone derivatives (those containing at least one hydrogen bond donor group) were all found to be modified in the presence of tetrabuthylammonium fluoride. On the other hand, only the spectra of 1,2- and 1,8-anthraquinone were seen to undergo a discernable change when exposed to tetrabutylammonium chloride in this same solvent. Presumably, the fluoride ion, in contrast to the chloride ion, is a strong enough hydrogen-bond acceptor that it can interact with anthraquinone derivatives that contain only a single hydrogen-bond donor group or single accessible donor group.

Significant bathochromic shifts in the absorption spectra were also observed for 1,2- and 1,8-diaminoanthraquinone in dichloromethane in the presence of chloride, bromide, and phosphate ions. These spectral changes were particularly dramatic in the case of 1,2-diaminoanthraquinone, being

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