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New Series of 1:1 Layered Complexes of α,ω-Dinitriles and Urea

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Since their first discovery by Bengen and Schlenk,[1] urea inclusion compounds have been studied widely and remain a topic of active research. We have used them as a tool for studying the interactions between functional group pairs[2] that are isolated in the linear, hexagonal channels.[3] With urea complexes of aliphatic α,ω-dinitriles we have noticed dramatic habit changes in crystals grown from methanol as the methylene chain is shortened from 10 carbon atoms to 3. With $NC(CH_2)_{10}CN$, the crystals exhibit the hexagonal needle form characteristic of channel inclusion compounds.[1] Crystals of $NC(CH_2)_6CN$/urea are chunky hexagonal prism/pyramids, while $NC(CH_2)_8CN$/urea form hexagonal-shaped plates. Complexes of $NC(CH_2)_5CN$ give large monoclinic plates, while those of $NC(CH_2)_4CN$ give chunky monoclinic prisms. When seeded with crystals formed by grinding (see below), solutions of $NC(CH_2)_3CN$ and urea also yield monoclinic plates.

Single-crystal and powder X-ray diffraction studies show that $NC(CH_2)_nCN$/urea crystals with $n = 6$, 8, and 10 are channel inclusion compounds.[4] Unlike the others, however, crystals of $NC(CH_2)_nCN$/urea with $n = 5$ (**1**), $n = 4$ (**2**), and $n = 3$ (**3**) are layered complexes that consist of sheets of hydrogen-bonded molecules, in which linear arrays of urea molecules are separated by dinitriles. The crystal packing of **2** is shown in Figure 1.[5] Atomic coordinates and atomic displacement parameters are given in Table I.

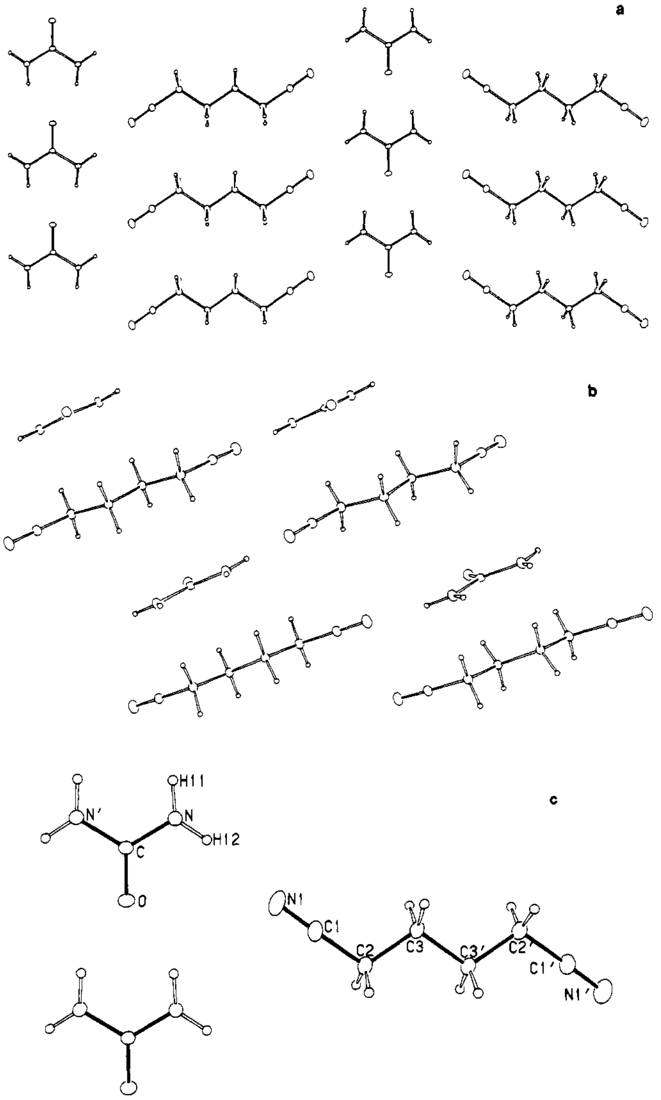

Figure 1. ORTEP view of the crystal packing of **2**. (a) View normal to hydrogen-bonded sheet (*b* vertical). (b) View of (010) (*a* horizontal) showing packing of hydrogen-bonded sheets. Selected intramolecular lengths (angstroms) and angles (degrees) N1–C1 1.136 (2), C1–C2 1.459 (2), O–C 1.238 (2), C–N 1.341 (1), N1–C1–C2 178.4 (2), O–C–N 121.5 (1). Hydrogen-bond lengths (angstroms) and angles (degrees): N···O (H11···O 2.07 (1), (N···O) 2.877 (2), N-H11···O 153.2 (9)); N···N1 (H12···N1 2.21 (1), N···N1 3.105 (1), N-H12···N1 171.2 (10)). (c) Numbering scheme.

Table I. Atomic Coordinates ($\times 10^5$) and Gaussian Parameters ($\times 10^4$) of 2[a]

atom	*x*	*y*	*z*	U_{eq}, Å^2
O	75000	−24794 (22)	−25000	467 (3)
C	75000	−51836 (31)	−25000	326 (4)
N	63817 (10)	−67138 (22)	−20939 (9)	440 (3)
N1	40211 (13)	−23885 (32)	−12778 (12)	804 (5)
C1	31220 (13)	−9280 (31)	−9529 (12)	537 (4)
C2	19444 (12)	8772 (29)	−5291 (11)	487 (3)
C3	5866 (11)	−9442 (26)	−2565 (10)	417 (3)

[a] The equivalent isotropic Gaussian parameter $U_{eq} = {}^1/_3\sum_{i=1}^{3} r_i^2$, where r_i are the root-mean-square amplitudes (principal components) of the Gaussian ellipsoid. Those parameters without an esd were not refined.

In the layered structures, the linear arrangement of urea molecules is reminiscent of the packing in tetragonal urea itself[7] and matches the hydrogen bonding motif found in *N,N'*-dicyclohexylurea[8] and *N,N'*-diphenylurea.[9] This translational motif, which contains two excess N–H protons per molecule, provides an ideal hydrogen-bonding template for the dinitriles, whose methylene chains can interleave to form a two-dimensional layer. The network thus formed is organized according to the rules for hydrogen bonding in crystals recently outlined by Etter[10] and

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(1) (a) Schlenk, W. *Justus Liebigs Ann. Chem.* **1949**, *565*, 204. (b) Bengen, M. F.; Schlenk, W. *Experientia* **1949**, *5*, 200.

(2) Hollingsworth, M. D.; Cyr, N. *Mol. Cryst., Liq. Cryst.* **1990**, *187*, 135.

(3) Smith, A. E. *Acta Crystallogr.* **1955**, *5*, 224.

(4) The crystal structure of $NC(CH_2)_8CN$/urea shows a unique zigzag channel arrangement for this commensurate inclusion compound. Details of this structure will be published elsewhere.

(5) **2**: $C_6H_8N_2 \cdot CH_4N_2O$ (dec, 109–119 °C), monoclinic, $P2/n$ (alternative setting for $P2/c$), $a = 8.889$ (4), $b = 4.578$ (2), $c = 11.448$ (4) Å, $\beta = 96.48$ (3)°, $V = 462.9$ Å^3, $\rho_{calc} = 1.206$ g cm^{-3}, $Z = 2$, λ (Mo Kα, graphite monochromator) = 0.71073 Å, 8189 reflections ($\theta_{max} \leq 35°$, entire Ewald sphere, −20 °C, Enraf-Nonius CAD4) were averaged over $2/m$ symmetry to give 2248 averaged observations, of which 1319 reflections with $I > \sigma(I)$ were used in the final cycles of refinement. The structure was solved by direct methods (MITHRIL).[6] Non-hydrogen atoms were refined with anisotropic Gaussian displacement parameters, and hydrogen atoms with isotropic terms and no restrains in the final cycle; goodness of fit = 1.72, $R_F = 0.054$, $R_{WF} = 0.062$. The highest peak in the final difference Fourier map has a density of 0.16 (5) e Å^{-3}. See the supplementary material section for further details.

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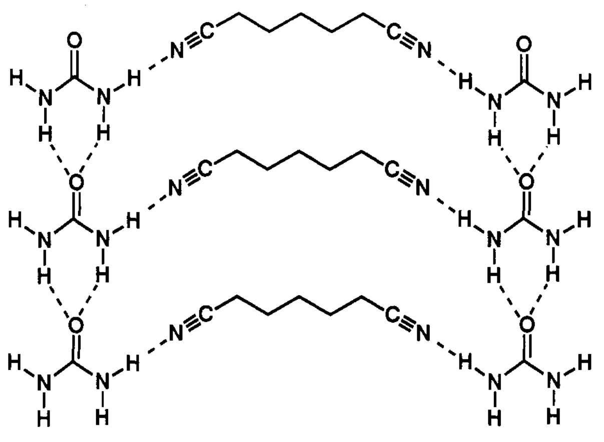
matches the recently reported layered structures of ureylenedicarboxylic acids,[11] which pack according to the same rules.

The two-dimensional sheet structures of **1** and **3**[12] are very similar to that of **2**, except that in the former structures the urea molecules all point in the same direction (see I), while in **2** the rows of urea molecules alternate directions within a layer. The formation of polar or nonpolar layers is simply a consequence of the parity of the dinitriles and the propensity to form linear C≡N- - -H—N hydrogen bonds.[13] In all three structures, adjacent layers are held together by dipolar and van der Waals forces; to achieve complete cancellation of dipoles, alternate layers in **1** and **3** point in opposite directions along the carbonyl axis of the urea molecule. In **2**, where alternation already exists within a layer, the layers are simply offset by the *n* glide, with no translation along *b*. The relatively weak interlayer forces and the hydrogen bonding within the layers give rise to the flat plate morphologies of **1** and **3**.



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The difference in packing with urea for long- and short-chain dinitriles presumably arises from a competition between nitrile–urea hydrogen bonding (which favors cocrystal formation) and van der Waals interactions of CH_2 groups with their surroundings (which seem to favor channel inclusion compound formation). (Secondary interactions between distant heteroatoms may also play a role, but lattice energy calculations suggest that the differences in Coulombic terms between **1** and **3** are small.) Within a layer, the 4.58-Å spacing along the carbonyl axis is controlled by the hydrogen-bonding requirements of the urea, and methylene groups are byond van der Waals contact in **1**–**3**. The notion that this monoclinic packing of methylene groups is inefficient[14] is borne out by comparison of the unit cell volumes of **3** (419.6 Å^3, extrapolated value at room temperature) and **1** (520.6 Å^3 at room temperature), which have virtually the same interlayer spacing and offset between urea molecules. The difference of 101.0 Å^3 yields a volume increment of 25.3 Å^3 per methylene, which is significantly larger than the increment of 23 Å^3 found for linear hydrocarbon chains that pack in the triclinic motif.[15,16] Calorimetric studies of channel inclusion compounds of alkanes with urea indicate that each methylene group of the guest is stabilized by a 2.7 kcal mol^{-1} interaction with the channel wall.[17] With longer chain lengths, this stabilization evidently overwhelms the factors that favor cocrystal formation.

Our attempts to grow (1:1) cocrystals of other short-chain dinitriles and urea from methanolic solutions have yielded crystals of dinitriles or urea (or both) but not cocrystals. However, forcefully grinding urea with fumaronitrile gives significant amounts of cocrystals, as shown by comparison of the powder X-ray diffraction patterns and IR spectra of the ground mixtures with those of the pure solid components and with those of complexes of **1** and **2** grown from solution.[18] (Crystallization from the melt does not yield cocrytals of fumaronitrile and urea.) Powder X-ray diffraction experiments show that cocrystals of **1**–**3** are formed in >98% yield by grinding the dinitriles with urea or in varying amounts by cooling melted mixtures.[19,20] The nitrile stretching frequencies of the complexed nitriles were higher than those of the uncomplexed nitriles by 4–6 cm^{-1}, as expected for hydrogen-bond formation.[21]

Since layered complexes of unsaturated systems hold considerable promise for topochemical polymerization,[22] we are presently exploring the use of the dinitrile–urea packing motif for the formation of crystallographically ordered polyacetylenes and polydiacetylenes containing cyanomethylene groups and other hydrogen-bond acceptors. Our ability to control the polarity of the layers should also have implications in the design of acentric materials for nonlinear optical applications. The studies of packing efficiency outlined above represent the first step in the rational design of cocrystals in this series.

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(12) An analysis of the packing and crystal structures of **1** and **3** will be reported in a forthcoming publication. Pertinent data for these structures are given here: **1** at room temperature: monoclinic, space group *P*2/*c* (*Z* = 2), *a* = 7.196 (2), *b* = 4.583 (3), *c* = 15.973 (4) Å, β = 98.769 (21)°, *V* = 520.6 Å^3. **3** at −60 °C: orthorhombic, space group *Pmmn* (*Z* = 2), *a* = 6.5020 (16), *b* = 13.712 (3), *c* = 4.5693 (10) Å, *V* = 407.5 Å^3. For **3**, four sets of cell constants obtained from −80 to −40 °C were extrapolated to room temperature for comparison of cell volumes.

(13) See, for example: (a) Legon, A. C.; Millen, D. J.; Rogers, S. C. *Proc. R. Soc. London, Ser. A* **1980**, *A370*, 213. (b) Bevan, J. W.; Legon, A. C.; Millen, D. J.; Rogers, S. C. *Proc. R. Soc. London, Ser. A* **1980**, *A370*, 239.

(14) Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1961; p 181.

(15) (a) Comparison of cell volumes for 11-bromoundecanoyl alkanoyl peroxide (where alkanoyl = decanoyl, lauroyl, and myristoyl) at 175 K gives an average increment of 23.3 ± 1.3 Å^3 per CH_2. See: Bertman, S. B. Ph.D. Thesis, Yale University, New Haven, CT, 1990. (b) For diundecanoyl peroxide and bis(tridecanoyl) peroxide at room temperature, the increment is 22 Å^3. See: McBride, J. M.; Bertman, S. B.; Cioffi, D. Z.; Segmuller, B. E.; Weber, B. A. *Mol. Cryst. Liq. Cryst.* **1988**, *161*, 1. Segmuller, B. E. Ph.D. Thesis, Yale University, New Haven, CT, 1982. Older estimates (von Sydow, E. *Ark. Kemi* **1956**, *9*, 231) are close to 23 Å^3 for polyethylene and *n*-hydrocarbons.

(16) The methods of Gavezzotti (Gavezzotti, A. *Nouv. J. Chim.* **1982**, *6*, 443) show that as the number of methylenes increases, the average electronic density (D_e) of the 1:1 complexes decreases more rapidly than expected from the linear relationship between D_e and the average atomic number for the contents of the unit cell. Our crystal structure of NC-$(CH_2)_8$CN/urea shows that by this method, this channel structure is packed more efficiently than the layered complexes, in agreement with our predictions.

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(18) See: Etter, M. C.; Frankenbach, G. M. *Chem. Mater.* **1989**, *1*, 10 and references therein for examples of cocrystal formation through grinding.

(19) To form the crystals by grinding we used a Wig-L-Bug, in which a steel cylinder (internal length = 22.5 mm, internal dia. = 11 mm) containing two steel ball bearings (6.3 mm diameter, 1.06 g) traversed a 17-mm pendular path (along the cylinder axis) at 10 Hz. Over a 10-min grinding period, the cylinder temperature rose from 20 to 46 °C. With **1**–**3**, cocrystal formation was virtually complete after two 10-min runs. Cocrystals were grown from methanol by slowly cooling a solution of 1.8 M urea (20–5 mL) containing 1–2 g of dinitrile from 30 to 5 °C or by evaporation of methanol at 5 °C.

(20) Our powder X-ray diffraction and IR studies also show that channel inclusion compounds are formed when urea is ground with suberonitrile.

(21) Grundnes, J.; Klaboe, P. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Interscience Publishers: New York, 1970; pp 134ff.

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Registry No. **1**, 131276-33-0; **2**, 22584-02-7; **3**, 131276-32-9; NC(CH$_2$)$_6$CN/urea, 131276-34-1; NC(CH$_2$)$_8$CN/urea, 131276-35-2; NC(CH$_2$)$_{10}$CN/urea, 25681-95-2.

Supplementary Material Available: Tables of bond distances, bond angles, torsional angles, weighted least-squares planes, hydrogen atom coordinates with *U*'s, and anisotropic and equivalent Gaussian parameters (6 pages); tables of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Organometallic Compounds as Luminescent Probes in the Curing of Epoxy Resins

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Epoxy resins possess many attractive features desirable in various electronic applications, such as adhesives, matrix resins for dielectrics, encapsulants, and protective coatings.[1] In all of these applications the polymer undergoes chemical and physical changes throughout the process in forming the final product; these changes have been monitored by a number of physicochemical methods in order to provide a better understanding of the cure process.[2] In contrast to these techniques, a number of reports have described the use of various fluorescent probes to monitor changes in matrix viscosity during thermal cross-linking or photo-cross-linking reactions.[3] Indeed, as early as 1956 Oster and Nishijima characterized a fluorescent probe sensitive to the rigidity of a polymer into which it is incorporated; they concluded that auramine O undergoes internal quenching when the two phenylene residues lose their coplanarity in the excited state and that an increase in the medium rigidity hinders this quenching mechanism.[3d] Furthermore, several studies have specifically addressed the importance of fluorescence techniques to monitor (in situ) the cross-linking reactions of epoxies.[3e,4] The fluorescence measurements reported in these studies relate to either measurements of fluorescence depolarization, excimer fluoresence or fluorescence quenching of the probing molecule due to the increase in the viscosity of the medium.

The present study deals with an entirely new approach to this problem. We demonstrate here that a series of transition-metal complexes with the general formula *fac*-XRe(CO)$_3$L [X = Cl, Br, I; L = 1,10-phenathroline (phen), 4,7-diphenyl-1,10-phenanthroline (Ph$_2$-phen), 4-methyl-1,10-phenanthroline (Me-phen), and 4,4'-dimethyl-2,2'-bipyridine (Me$_2$-bpy)] readily exhibit luminescence in an epoxide/anhydride system and that this luminescence varies greatly as the resin is heated and cured. These organometallic compounds possess a number of properties that facilitate utilizing them as spectroscopic probes to monitor polymerization reactions.

Complexes of the type *fac*-XRe(CO)$_3$L have been previously found to be strongly emissive both in room-temperature fluid solution and as a low-temperature glassy solution at 77 K. These emissions are associated with a lowest lying metal-to-ligand charge-transfer (MLCT) excited state in which electronic transitions take place from a metal-centered molecular orbital to a ligand-localized π^* orbital.[5] The luminescence characteristics of these *fac*-XRe(CO)$_3$L complexes are particularly sensitive to solvent changes and environmental rigidity; specifically, a more intense, longer lived, and substantially blue-shifted emission is observed when these solutions become frozen. This effect has been referred to as "luminescence rigidochromism"[5a,6] and is understood to arise from the variations that take place in the interaction of the polar excited molecular species with the local dipoles in the surrounding medium.[7] In this study we make use of this effect, not in the context of solution freezing, but to monitor the changes that take place in the matrix during the curing process of a model cycloaliphatic diepoxide resin.

fac-XRe(CO)$_3$L compounds were synthesized by refluxing XRe(CO)$_5$ with the appropriate ligand in benzene according to a procedure described previously.[7b] The model epoxide/anhydride system was prepared by combining 50 g of (3,4-epoxycyclohexyl)methyl 3,4-epoxycyclohexanecarboxylate (Union Carbide ERL-4221) with 50 g of *cis*-cyclohexanedicarboxylic anhydride. To this mixture was added 0.5 g of benzyldimethylamine, 1.0 g of ethylene glycol, and 0.004 g of the *fac*-XRe(CO)$_3$L probe material. This formulation was placed in a 30 mm × 30 mm × 1 mm reaction cell constructed of a silicone rubber gasket sandwiched between two glass microscope slides. The epoxide was heated in an oven maintained at 120 °C; the curing temperature was carefully monitored by utilizing a recording thermocouple. Emission spectra were collected on a SLM Instruments Model 8000/8000S spectrometer that incorporates a red-sensitive Hamamatsu R928 photomultiplier and photon counting detection capabilities. Spectra were obtained by orienting the reaction cell at an angle of 20° to the incident light. Emission lifetimes were recorded on a PRA System 3000 time-correlated pulsed single-photon counting apparatus in an identical configuration.

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