is preserved. The vibrations at 2090 and 1785 cm^{-1} (2100 and 1795 cm^{-1} for **3c**) correspond respectively to a terminal and a bridging carbonyl group; the former is further coordinated to the Rh atom that does not bear the amino phosphane ligand (in the case where the CO and amino phosphane are coordinated on the same Rh atom, a lower value of $\nu(\text{C}{=}\text{O})$, close to those measured for **4** or **2**, is expected). Coordination of the alkynes is shown by the presence of the $\nu(\text{C}{\equiv}\text{C})$ vibration at 1550 cm^{-1} (1575 cm^{-1} for **3c**), in the region generally attributed to alkynes bridging two Rh atoms in the coordination modes μ-η^1,η^1 [5,6] and μ-η^2,[7] and as such, IR spectroscopy does not allow distinction between these two coordination modes. Higher values for the $\nu(\text{C}{\equiv}\text{C})$ vibration, from 1850 to 1950 cm^{-1}, are found for alkynes π-coordinated to one rhodium center only,[8] thus excluding such a structure for the materials isolated here.

The poor solubility and poor stability of **3b,c** prevented us from measuring satisfactory ^{13}C NMR spectra, even at 100.62 MHz on a Bruker WM 400 spectrometer with a S/N ratio sufficient to detect with confidence the Rh–C couplings, which would have allowed us to distinguish unambigously between structures **3** and **3′**. However, the ^{1}H, ^{31}P, and ^{19}F NMR data could be collected for **3b,c**, but not for **3a**, whose solubility is very low and is further accompanied by decomposition. The ^{31}P NMR spectra of **3b,c** consist respectively of a doublet of doublets centered at 147 ppm ($^1J_{\text{P-Ph}}$ = 230 Hz, $^xJ_{\text{P-Rh}}$ = 9 Hz) and of a complex doublet at 145 ppm ($^1J_{\text{P-Rh}}$ = 220 Hz) due to additional coupling with the ^{19}F nuclei. The largest coupling constants indicate P-coordination. In the case of **3b**, assignment of the other coupling constant to $^3J_{\text{P-Rh}}$ through a Rh–Rh bond is only tentative, as high-order coupling constants have been measured for dinuclear Rh species in which no such bonds occur.[9] More informative, the ^{19}F NMR spectrum of **3c** exhibits a complex multiplet at −50.6 ppm and a doublet of quadruplets at −53 ppm ($J_{\text{F-F}}$ = 12 Hz; $J_{\text{F-Rh}}$ = 3 Hz) in a 1/1 ratio. This pattern and, particularly, the different fine structures for the two F resonances favor the less symmetrical structure **3c** with respect to the almost symmetrical structure **3′c** (for which identical fine structures would have been expected for each CF$_3$ group).

Action of the Strong Nucleophiles MeLi and Ph$_2$PLi. The action of MeLi or Ph$_2$PLi on **1** provokes the cleavage of the chloro bridge: from the reaction mixture, only the known mononuclear complex **4**[1] could be isolated (60% yield).

Action of Other Small Molecules. A rapid reaction with total consumption of **1** is observed with SO$_2$ or (CN)$_2$C=C(CN)$_2$ (TCNE) in toluene, but all attempts to isolated any pure compound have so far failed.

No reaction of **1** is observed with an excess of O$_2$, CO, CO$_2$, CS$_2$, or MeI or of unactivated or moderatively activated alkenes (H$_2$C=CH$_2$, H$_2$C=CHCN, Me$_2$C=CMe$_2$) under thermal or photolytic conditions at atmospheric pressure.

Conclusions

The main feature of this study is the unexpected inertia of the singly bridged dissymmetric binuclear rhodium complex **1**. Its absence of reactivity toward O$_2$, CO, CO$_2$, and MeI is surprising, as is its limited tendency to add alkenes and alkynes and form additional bridges, which occurs only with the most strongly activated ones to yield the μ-CO, μ-Cl, and μ-η^1,η^1 triply bridged species **3**. The stability of the single chloro bridge in **1** is illustrated by the fact that it is preserved in the presence of *t*-BuNC, which leads to the substitution of the two carbonyl groups located on the same metal center. To cleave this bridge requires an excess of *t*-BuNC, an excess of the bidentate P/N ligand,[1] or the action of strong nucleophiles such as MeLi and Ph$_2$PLi.

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A 1,1-Dithiocarboxylate Ligand with an Easily Derivatizable Group. Synthesis and Structure of Tris[2-(ethylamino)cyclopent-1-ene-1-dithiocarboxylato]bismuth(III)

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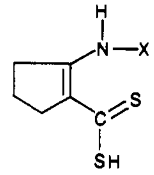
Received October 31, 1986

1,1-Dithio ligands (dithiocarbamates, dithiophosphates, dithioxanthates, dithiocarboxylates) have been the subject of intense investigation over the last two decades.[1] Most studies are concerned with transition-metal complexes of 1,1-dithio ligands having only alkyl or aryl substituents. Only a few examples of complexes of 1,1-dithio ligands are known in which the ligand has free functional groups not involved in coordination.

2-Aminocyclopent-1-ene-1-dithiocarboxylic acid (ACDA), a compound having antifungal properties,[2] forms complexes[3,4] with transition metals (Ni(II), Pt(II), Pd(II), Mo(VI)) that were believed to be monomeric, neutral species with S,S rather than N,S bonding to the metal. However, no crystallographic information on any of these complexes was obtained because of their limited solubility in common organic solvents. However, it is easy to derivatize the amine group of the ligand by transamination reactions to give species having a variety of substituents at the nitrogen atom. These derivatives give complexes with improved solubility characteristics. As part of a research program to develop a radiopharmaceutical that can bind strongly to both Pb(II) and Bi(III) and, in addition, have latent functionality to bind to a suitable carrier, we have prepared and determined the crystal structure of the Bi(III) complex of 2-(ethylamino)cyclopent-1-ene-1-dithiocarboxylic acid (EACDA). This also appears to be the first crystal structure of a dithiocarboxylate complex with a non transition metal that has been reported.



X = H (ACDA)
X = C$_2$H$_5$ (EACDA)

Experimental Section

Chemicals Used. All of the reagent grade chemicals were purchased from Aldrich Chemical Co. and were used without further purification. Anhydrous BiCl$_3$ was 98% pure.

1. Preparation of 2-Aminocyclopent-1-ene-1-dithiocarboxylic Acid (ACDA). ACDA was prepared by following a published procedure.[3] Yield: 65% (mp 97–98 °C (lit.[3] 98 °C)).

2. Preparation of 2-(Ethylamino)cyclopent-1-ene-1-dithiocarboxylic Acid (EACDA). EACDA was prepared from ACDA by a transamination reaction with ethylamine following a published procedure.[2b] The product was recrystallized from acetone. Yield: 81%. (mp 111–112 °C (lit.[2b] 111 °C)).

3. Preparation of Bi(III) Complexes. (a) With ACDA. Complex I. An ethanolic solution of anhydrous BiCl$_3$ (0.32 g; 1 × 10^{-3} mol) (10 mL) was added slowly with constant stirring at room temperature to an ethanolic solution (10 mL) of ACDA (0.48 g; 3 × 10^{-3} mol). The bismuth complex was obtained immediately as an orange precipitate. The pre-

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Table I. Crystal and Refinement Data

formula	$BisS_6N_3C_{24}H_{36}$
fw	767.909
a, Å	10.835 (4)
b, Å	14.854 (4)
c, Å	18.936 (5)
β, deg	105.98 (2)
V, Å^3	2930.0 (10)
space group	$P2_1/c$
Z	4
no. of reflcns used to determine cell const	15
d_{calcd}, g/cm^3	1.74
λ(Mo K_α), Å	0.71069
monochromator	graphite
linear abs coeff, cm^{-1}	61.50
cryst dimens, mm	0.16 × 0.19 × 0.24
transmissn factor range	$0.22 < T < 0.48$
diffractometer	Syntex $P2_1$
daa collcn method	ω-scan
2θ range, deg	$0 \leq 2\theta \leq 50$
temp., K	130 (1)
ω-scan range, deg	1.0
wt scheme[a]	$w = 1/[(\sigma^2(F_o) + gF_o^2]$
no. of std reflcns	2
% variation in std intens	$<\pm 0.1$
octants collcd	$+h,+k,\pm l$
no. of unique data collcd	5163
no. of data used in refinement	4318
R(MERGE)[b]	0.000
data:param ratio	~14
final GOF	1.87
final R_f	0.0287
final R_{wF}	0.0306
syst absences	$0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$
final largest shift/esd	0.046
highest peak in final diff map, e/Å^3	0.58

[a] *g* was refined by fitting $(F_0 - F_c)^2$ to $[\sum(F) + (\text{abs}(g))F^2)/K]^2$ (where *K* is a scale factor) to put the weight on an approximately absolute scale. For the present structure $g = 0.00021$ and $K = 1.00428$. [b] $R(\text{MERGE}) = (\sum(N)\sum(w(F(\text{mesn}) - F)^2))/\sum((N-1)\sum(wF^2)))^{1/2}$, where the inner summations are over the *N* equivalent reflections averaged to give *F*(mean) and the outer summations are over all unique observed reflections.

cipitate was washed several times with ethanol and air-dried. Yield: 99%. The precipitate is sparingly soluble in DMF and Me_2SO but insoluble in all other common organic solvents.

(b) With EACDA. Complex II. In a typical experiment an ethanolic solution (10 mL) of $BiCl_3$ (0.32 g; 1×10^{-3} mol) was allowed to react slowly at room temperature with constant stirring with an ethanolic solution (10 mL) of EACDA (0.56 g; 1×10^{-3}). Immediately, a red solid precipitated, which was collected by filtration, washed several times with ethanol, and air-dried. Yield: 98%. The red solid was moderately soluble in common organic solvents. Red single crystals as rectangular plates suitable for X-ray crystallography could be grown by slow evaporation at room temperature of a solution of the compound in THF.

The red bismuth complex could also be isolated in a ~90% yield when an ethanolic solution of excess EACDA (5 mol) was allowed to stir at room temperature with a slurry of BiOCl (1 mol) in ethanol. Single crystals could be grown from the solution of the red complex dissolved in THF by slow evaporation. This compound was found to be identical with the one above as it had the same unit cell dimensions and the same space group.

X-ray Diffraction Studies. A crystal of $Bi(H_{-1}EACDA)_3$ was mounted at the end of a glass fiber. All diffraction measurements were made at 130 K with a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation. Intensity data were collected by ω-scan technique and corrected for decay, absorption,[8] and *Lp* effects. Details of data collection and refinement are given in Table I.

Table II. Fractional Atom Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^3)

atom	*x*	*y*	*z*	U_{eq}[a]
Bi	783 (1)	6471 (1)	5836 (1)	18 (1)
S(1)	1959 (1)	4980 (1)	5069 (1)	22 (1)
S(2)	3080 (1)	5839 (1)	6532 (1)	23 (1)
S(3)	−1211 (1)	6324 (1)	6689 (1)	24 (1)
S(4)	1237 (1)	7365 (1)	7078 (1)	23 (1)
S(5)	−579 (2)	8124 (1)	5168 (1)	34 (1)
S(6)	2099 (2)	7602 (1)	5270 (1)	29 (1)
N(1)	3960 (4)	3601 (3)	4941 (2)	25 (2)
N(2)	−2764 (4)	7089 (3)	7651 (3)	24 (2)
N(3)	−1227 (5)	9591 (4)	4038 (3)	42 (2)
C(1)	3225 (5)	5095 (4)	5829 (3)	16 (2)
C(2)	4406 (5)	4659 (4)	5964 (3)	18 (2)
C(3)	5536 (5)	4860 (4)	6620 (3)	24 (2)
C(5)	6061 (5)	3616 (4)	5892 (3)	28 (2)
C(6)	4729 (5)	3949 (4)	5548 (3)	22 (2)
C(7)	4349 (5)	2859 (4)	4534 (3)	37 (2)
C(8)	4160 (7)	1925 (5)	4833 (5)	67 (4)
C(9)	−288 (5)	7151 (4)	7206 (3)	18 (2)
C(10)	−626 (5)	7674 (4)	7734 (3)	18 (2)
C(11)	242 (5)	8375 (4)	8202 (3)	24 (2)
C(12)	−679 (5)	8949 (4)	8506 (3)	30 (2)
C(13)	−1813 (5)	8347 (4)	8500 (3)	26 (2)
C(14)	−1796 (5)	7653 (4)	7922 (3)	20 (2)
C(15)	−4002 (5)	7135 (4)	7836 (3)	31 (2)
C(16)	−4919 (6)	7803 (4)	7356 (4)	40 (3)
C(17)	763 (6)	8291 (4)	8469 (3)	28 (2)
C(18)	903 (7)	8898 (4)	4344 (3)	36 (2)
C(19)	2079 (7)	8984 (5)	4056 (4)	44 (3)
C(20)	1873 (7)	9886 (5)	3634 (4)	57 (3)
C(21)	419 (7)	10052 (5)	3411 (4)	54 (3)
C(22)	−59 (7)	9506 (4)	3955 (3)	38 (3)
C(23)	−2180 (7)	10221 (5)	3597 (4)	53 (3)
C(24)	−3374 (7)	10164 (5)	3866 (4)	62 (3)
C(4)	6636 (5)	4266 (4)	6520 (3)	25 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

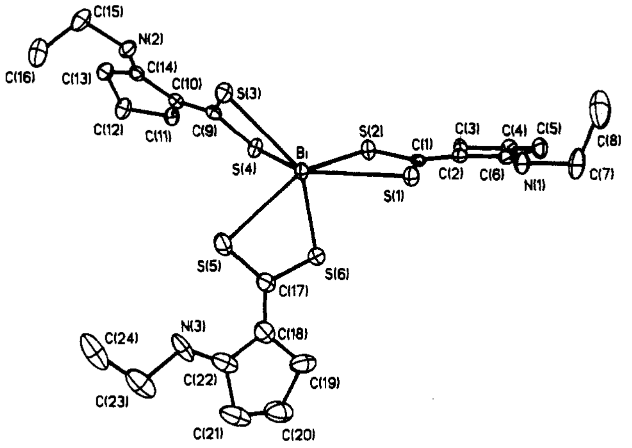

Figure 1. ORTEP view of the title complex showing the atom-numbering scheme. Hydrogen atoms have been omitted for clarity.

The structure was solved by the heavy-atom method and refined on *F* by a full-matrix least-squares technique using the SHELX81 program package.[9] The bismuth atom could be located from the Patterson map. The remaining non-hydrogen atoms were located from successive difference Fourier maps. Several H atoms could be located in the difference map at the isotropic convergence. However, coordinates of all H atoms were calculated by assuming an idealized geometry with C–H bond lengths of 0.96 Å and added to the atom list. H atom temperature factors were set as $U(H) = 1.2U_{eq}(C)$, where $U_{eq}(C)$ is the equivalent isotropic thermal parameter of the C atom to which the H atom is bonded. Hydrogen atom parameters were not refined. Anisotropic refinement of all non-hydrogen atoms led to convergence with $R_F = 0.0287$ and $R_{wF} = 0.0306$. Corrections for anomalous dispersion were applied to all at-

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(8) Program XABS by H. Hope and B. Moezzi; the program obtains an absorption tensor from F_o–F_c differences. When absorption corrections are performed numerically by using the indexed faces and crystal dimensions, a final value of R_F of 0.037 is obtained.

(9) Crystallographic programs used were those of SHELXTL, version 4, installed on a Data General Eclipse computer.

Table III. Bond Distances (Å) and Angles (deg) in Complex II

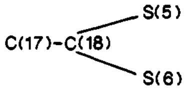
Bi–S(1)	3.108 (2)	B–S(5)	2.963 (2)
Bi–S(2)	2.647 (1)	Bi–S(3)	3.040 (1)
Bi–S(6)	2.617 (2)	Bi–S(4)	2.626 (1)
S(2)–C(1)	1.770 (6)	S(1)–C(1)	1.701 (5)
S(4)–C(9)	1.763 (6)	S(3)–C(9)	1.712 (5)
S(6)–C(17)	1.764 (6)	S(5)–C(17)	1.717 (7)
N(1)–C(7)	1.470 (8)	N(1)–C(6)	1.325 (6)
N(2)–C(15)	1.478 (8)	N(2)–C(14)	1.331 (7)
N(3)–C(23)	1.471 (8)	N(3)–C(22)	1.323 (10)
C(2)–C(3)	1.514 (7)	C(1)–C(2)	1.394 (7)
C(3)–C(4)	1.536 (8)	C(2)–C(6)	1.417 (8)
C(5)–C(4)	1.526 (8)	C(5)–C(6)	1.495 (7)
C(9)–C(10)	1.394 (8)	C(7)–C(8)	1.534 (10)
C(10)–C(14)	1.409 (8)	C(10)–C(11)	1.514 (7)
C(12)–C(13)	1.517 (8)	C(11)–C(12)	1.540 (9)
C(15)–C(16)	1.518 (8)	C(13)–C(14)	1.506 (8)
C(18)–C(19)	1.523 (11)	C(17)–C(18)	1.381 (9)
C(19)–C(20)	1.544 (10)	C18)–C(22)	1.422 (9)
C(21)–C(22)	1.511 (10)	C(20)–C(21)	1.534 (11)
		C(23)–C(24)	1.518 (12)

S(1)–Bi–S(2)	61.9 (4)	S(5)–Bi–S(6)	53.7 (3)
S(1)–Bi–S(3)	129.8 (5)	S(1)–Bi–S(5)	127.6 (4)
S(3)–Bi–S(4)	63.0 (5)	S(3)–Bi–S(5)	86.8 (4)
S(2)–Bi–S(4)	79.4 (5)	S(2)–Bi–S(6)	83.6 (3)
S(4)–Bi–S(6)	93.0 (4)	Bi–S(2)–C(1)	96.5 (2)
Bi–S(4)–C(9)	94.6 (2)	Bi–S(6)–C(17)	94.2 (2)
C(6)–N(1)–C(7)	123.0 (5)	C(14)–N(2)–C(15)	123.3 (5)
C(22)–N(3)–C(23)	122.6 (6)	S(1)–C(1)–S(2)	118.8 (3)
S(1)–C(1)–C(2)	126.5 (4)	S(2)–C(1)–C(2)	114.7 (4)
C(1)–C(2)–C(3)	123.6 (5)	C(1)–C(2)–C(6)	126.7 (4)
C(3)–C(2)–C(6)	109.6 (4)	C(2)–C(3)–C(4)	105.4 (5)
C(6)–C(5)–C(4)	105.6 (5)	N(1)–C(6)–C(2)	125.5 (5)
N(1)–C(6)–C(5)	123.4 (5)	C(2)–C(6)–C(5)	111.1 (4)
N(1)–C(7)–C(8)	113.4 (6)	S(3)–C(9)–S(4)	118.2 (3)
S(3)–C(9)–C(10)	125.7 (4)	S(4)–C(9)–C(10)	116.1 (4)
C(9)–C(10)–C(11)	124.0 (5)	C(9)–C(110)–C(14)	127.0 (5)
C(11)–C(10)–C(14)	108.9 (5)	C(10)e–C(11)–C(12)	103.7 (4)
C(11)–C(12)–C(13)	106.2 (5)	C(12)–C(13)–C(14)	103.7 (5)
N(2)–C(14)–C(10)	125.8 (5)	N(2)–C(14)–C(13)	123.0 (5)
C(10)–C(14)–C(13)	111.1 (5)	N(2)–C(15)–C(16)	112.1 (5)
S(5)–C(17)–S(6)	116.3 (3)	S(5)–C(17)–C(18)	127.0 (5)
S(6)–C(17)–C(18)	116.7 (5)	C(17)–C(18)–C(19)	125.5 (6)
C(17)–C(18)–C(22)	125.3 (7)	C(19)–C(18)–C(22)	109.1 (6)
C(18)–C(19)–C(20)	104.0 (6)	C(19)–C(20)–C(21)	105.8 (6)
C(20)–C(21)–C(22)	104.2 (5)	N(3)–C(22)–C(18)	126.0 (6)
N(3)–C(22)–C(21)	123.2 (6)	C(18)–C(22)–C(21)	110.7 (6)
N(3)–C(23)–C(24)	107.7 (6)	C(3)–C(4)–C(5)	107.1 (4)

oms.[10a] Neutral atom scattering factors were those of Cramer and Waber.[10b] Final atomic parameters are listed in Table II and a view of the structure is given in Figure 1. Lists of observed and calculated structure factors, anisotropic thermal parameters, and H atom coordinates are available.[5]

Results and Discussion

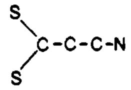
The Bi(H$_{-1}$EACDA)$_3$ complex can be prepared by treatment of either a solution of BiCl$_3$ or a suspension of BiOCl in ethanol with EACDA. The structure exhibits discrete neutral Bi($C_8H_{12}NS_2$)$_3$ species with S_6 ligand donor sets. The N atom is not coordinated to the Bi(III) ion as it is at least 5.808 Å away. Each of the C–CS$_2$ units is planar to within ±0.004 Å. The plane described by



(third ligand; Figure 1) makes an angle of 74.6° with the plane described by the same unit of the first ligand and an angle of 86.0° with the plane described by the second ligand. Thus, the coordination geometry around Bi(III) can be described as trigonal antiprismatic. Only one other structure of a Bi(III) 1,1-dithio complex, tris(diethyldithiocarbamato)bismuth(III) (Bi(Et$_2$Dtc)$_3$, has been reported and a similar coordination geometry is present in that complex.[6]

As also seen in the tris(diethyldithiocarbamate) complex, bismuth is coordinated asymmetrically by each dithio ligands in such a way that there are three short Bi–S bonds [Bi–S(2), 2.647 (1) Å; Bi–S(4), 2.626 (1) Å; Bi–S(6), 2.617 (2) Å] and three long Bi–S bonds [Bi–S(1), 3.108 (2) Å; Bi–S(3), 3.040 (5) Å; Bi–S(5), 2.963 (5) Å]. Thus, S(1), S(3), and S(5) and likewise S(2), S(4), and S(6) form triangular faces in the coordination polyhedron. The molecular symmetry around Bi(III) is closer to C_3. The asymmetric binding of the dithio ligands may be attributed to the presence of a stereochemically active lone pair on the Bi(III) ion. If the lone pair lies along the 3-fold axis, the S(1), S(3), and S(5) atoms on the same side as the lone pair are pushed away from the Bi(III) ion, resulting in longer Bi–S bond lengths.

The S–C–S bond angles, which range from 116.3 (3) to 118.8 (3)°, are also similar to those found in the diethyldithiocarbamate complex of Bi(III).[6,7] In contrast, when 1,1-dithio ligands are bound to metal ions in a symmetrical fashion (both M–S bonds equal in length), the S–C–S angles are shorter[7] (110 (1) to 113 (1)°), signifying greater strain at the sp^2 C atom. S–Bi–S bond angles are within 61.6–63.7° as found in other Bi(III) complexes.[6,11] The C–C bond lengths between the C atom of the CS$_2$ group and the one bonded to it lie between 1.394 (7) and 1.381 (9) Å, showing appreciable double bond character. The



group is slightly distorted from planarity (within ±0.014 Å). The S(1) atom from the nearest neighbour is 3.689 Å away from the Bi(III) ion of the original molecule, signifying a weakly bonded dimeric structure. This distance in this EACDA complex is much longer than the 3.389 Å distance found in the related diethyldithiocarbamate complex.

Further studies of complexes formed by derivatives of the H$_{-1}$ACDA ligand are in progress.

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates (2 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(10) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) pp 149–159; (b) pp 99–101.

(11) Bharadwaj, P. K. and Musker, W. K., to be submitted for publication.

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Time-Resolved Resonance Raman Spectra of Polypyridyl Complexes of Ruthenium(II)

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Time-resolved resonance Raman (TR^3) spectroscopy has recently evolved as a powerful tool for the investigation of the dynamics and structures of a variety of reactive intermediates, electronic excited states, biological systems, and enzyme–substrate

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