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The Characterization of Technetium Organohydrazide Chelate Complexes. The Synthesis of a Technetium Phenylimido Complex. The X-ray Crystal Structure of $[TcO(SC_6H_2Pr^i{}_3)_2(PhNNCON_2HPh)]$

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Abstract

The reaction of the neutral technetium(V) oxo tris(thiolate) complex $[TcO(SAr)_3(C_5H_5N)]$ with (phenylazo)formic acid 2-phenylhydrazide in methanol gives the oxo technetium(V) bis(thiolato) complex $[TcO(SAr)_2(PhN_2CONNHPh)]$ (2). The FAB-MS(+) of 2 shows the protonated parent ion and the organohydrazide ligand fragmenting such that the technetium–phenylimido species $[TcO(SAr)(NPh)]^+$ is generated. The X-ray crystal structure of 2 shows a distorted square pyramidal coordination geometry and the nitrogen-bound proton on the terminal exocyclic nitrogen of the singly deprotonated, chelated organohydrazide ligand. Crystal data for $C_{43}H_{56}N_4O_2S_2Tc$: triclinic space group $P\bar{1}$, $a = 13.3613(8)$, $b = 14.02768(6)$, $c = 13.0857(6)$ Å, $\alpha = 113.949(4)$, $\beta = 100.265(4)$, $\gamma = 76.019(4)°$, $V = 2166.0(4)$ Å^3 to give $Z = 2$. Structure solution and refinement based on 7786 reflections converged at $R = 0.040$, $R_w = 0.045$.

The reaction of the cationic technetium(V) oxo complex $(Bu_4N)[TcOCl_4]$ with (phenylazo)formic acid 2-phenylhydrazide and 1,5-diphenylcarbazide yields the phenylimido complex $[TcCl(NPh)(PhN_2CON_2HPh)_2]$ (1) which incorporates a phenylimido unit. The infrared spectrum of this species shows a strong band at 1204 cm^{-1} which has been assigned to ν(Tc=N). The fast atom bombardment mass spectrometric analysis shows the protonated parent ion and a fragmentation profile containing both bis(phenylimido) and tris(phenylimido) technetium species generated through the decomposition of the chelated organohydrazide ligands.

Introduction

Technetium has been shown to form multiple bonds with various nitrogenous donor ligands, forming stable nitrido [1], nitrosyl [2], and aryldiazenido cores [3]. Technetium oxo chemistry is also well established. However complexes which incorporate the organoimido core, (Tc=N–R), a species isoelectronic to the oxo species, have yet to be reported. The organic moiety on the imido unit might provide a method of 'fine-tuning' the properties of the complex and allow the manipulation of its biodistribution as related to technetium radiopharmacology. Organoimido complexes are known for all group IV through group VIII transition metals except technetium [4]. Preliminary results reported within describe the synthesis and characterization of a technetium complex which incorporates the organoimido unit.

Experimental

Caution: ^{99}Technetium is a weak β-emitter. All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsehwhere [5].

Ammonium pertechnetate was supplied as a gift from DuPont Biomedical Products. Reagents and solvents were used as received unless otherwise specified. Infrared spectra were obtained on a Mattson Cygnus 100 FTIR. Fast atom bombardment mass spectra of samples dissolved in a *p*-nitrobenzyl alcohol matrix were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerated voltage of 8 kV. The FAB gun produced a beam of 6–8 keV xenon neutrals. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Syntheses

$[TcCl(NPh)(PhNNCON_2HPh)_2]$ (1)

To an acetone solution of 0.12 g of $(Bu_4N)[TcOCl_4]$ was added 0.20 g of (phenylazo)formic acid 2-phenylhydrazide/1,5-diphenylcarbazide

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(Aldrich Chemicals, catalog no. 25,546-77) suspended in acetone. An immediate dark purple color developed with stirring at room temperature. The solution was warmed gently overnight. The acetone was removed by rotary evaporation leaving a deep purple residue which was dissolved in benzene and filtered through a cotton plug into a scintillation vial. The purple benzene solution was then carefully layered with pentane. Purple–green dichroic crystals form gradually at room temperature which desolvate with prolonged exposure to air. *Anal.* Calc. for $C_{32}H_{27}N_9O_2ClTc[\frac{1}{2}(H_2O)]$: C. 53.22; H, 4.06; N, 17.46. Found: C, 53.61; H, 4.15; N, 17.30%. FAB-MS(+): $m/z = 704$ $[MH]^+$, 668 $[M - Cl]^+$, 613 $[MH - NPh]^+$, 520 $[Tc(NPh)_2(PhN_2CONNHPh)H]^+$, 372 $[Tc(NPh)_3]^+$. IR (KBr): $\nu(Tc{=}N) = 1204\ cm^{-1}$, $\nu(N{=}N) = 1591\ cm^{-1}$, $\nu(N{-}H)$ 3250 cm^{-1}.

$[TcO(SC_6H_2Pr^i{}_3)_2(PhNNCON_2HPh)]$ (2)

A 0.10 g sample of $[TcO(SC_6H_2Pr^i{}_3)_3(C_5H_5N)]$ was suspended in 20 ml of methanol. To this was added 0.13 g (phenylazo)formic acid 2-phenylhydrazide suspended in 5 ml of methanol. The dull orange suspension gradually formed a red–purple solution with gentle warming. The suspension was warmed for 30 min and the resulting purple solid was isolated and washed with methanol. The purple solid was redissolved in dichloromethane and carefully layered with methanol. Purple–green dichroic crystals of 2 formed upon sitting overnight in a refrigerator. *Anal.* Calc. for $C_{43}H_{56}N_4O_2S_2Tc$: C, 62.65; H, 6.85; N, 6.83. Found: C, 62.45; H, 6.94; N, 6.91%. FAB-MS(+): $m/z = 825$ $[MH]^+$, 589 $[M - SAr]^+$, 441 $[TcO(NPh)(SAr)]^+$. IR (KBr): $\nu(N{=}N) = 1595\ cm^{-1}$, $\nu(N{-}H) = 3250\ cm^{-1}$, $\nu(Tc{=}O) = 950\ cm^{-1}$. UV–Vis ($CH_2Cl_2$): λ_{max} (nm) (ϵ (1 mol^{-1} cm^{-1})) 260 (1.85×10^4), 428 (7.68×10^3), 548 (1.97×10^4), 658 (4.74×10^3).

Results and Discussion

The literature contains a number of established methods for introducing the organoimido ligand. Among these are the deprotonation of primary amines [6], the use of silylamines [7] and the alkylation of nitrido complexes [8]. Various 1,2-disubstituted hydrazines have also been shown to fragment such that the phenylimido unit is retained in the metal complex. This method has been used to synthesize imido complexes of both molybdenum [9] and rhenium [10]. The latter technique has been employed to synthesize the technetium–phenylimido complex $[TcCl(NPh)(PhN_2CONNHPh)_2]$ from $(Bu_4N)[TcOCl_4]$ [11] and the 1,2-disubstituted, chelating hydrazine adduct (phenylazo)formic acid 2-phenylhydrazide and 1,5-diphenylcarbazide. These ligands have long been employed in photometric determinations of molybdenum [12]. The organohydrazido–molybdate complexes formed in these reactions have only recently been structurally characterized [13].

The technetium(V) oxo complex $(Bu_4N)[TcOCl_4]$ reacts with (phenylazo)formic acid 2-phenylhydrazide and 1,5-diphenylcarbazide $\{C_6H_5N{=}NCONHNHC_6H_5(C_6H_5NHNH)_2CO)$; 1,5-diphenylcarbazone compound with 1,5-diphenylcarbazide$\}$ in warm acetone to give purple–green dichroic crystals of $[TcCl(NPh)(PhNNCON_2HPh)_2]$ in 30% yield when recrystallized from benzene layered with pentane.

The ligands presumably coordinate in a bidentate manner, chelating through the carbonyl-oxygen and α-nitrogen atoms of the phenylazo organohydrazide (*vide infra*). The infrared spectrum of complex 1 shows a very strong band at 1204 cm^{-1} which has been tentatively assigned to the $\nu(Tc{=}N)$ from the phenylimido unit. This absorption falls within the range generally associated with this species, 1100–1300 cm^{-1} [4]. The spectroscopy however fails to establish the coordination mode of the phenylimido unit as linear or bent. As a rule, the imido moiety adopts the bent conformation (I) when the electron count of the 4-electron donating linear conformation (II) causes the complexes' electron count to exceed 18 electrons (see Fig. 1). Chloride ligands tend to occupy sites *trans* to the phenylimido unit, which has frequently been observed in rhenium phenylimido complexes. Examples of rhenium complexes with this ligand disposition include $[ReCl_3(NR)(PPh_3)_2]$ [14], $[ReCl(NR)(NH_2CH_3)_4]^{2+}$ [15] and $[ReCl(NR)(S_2CNR_2)_2]$ [6, 16]. The infrared spectrum of complex 1 shows no absorptions from the carbonyl groups of the organohydrazide chelate rings which is common for this type of organohydrazide coordination [8, 9]. The singly deprotonated bidentate organohydrazide ligands leave 'dangling' (N=N(H)–Ph) moieties which remain IR active. Absorptions assigned to $\nu(N{=}N)$ appear at 1591 cm^{-1}, while the N–H absorptions from these species appear at 3250 cm^{-1}.

The technetium(V) complex $[TcO(SC_6H_2Pr^i{}_3)_3(C_5H_5N)]$ [17] reacts with an excess of phenylazoformic acid 2-phenylhydrazide in methanol to give the five-coordinate $[TcO(SC_6H_2Pr^i{}_3)_2(PhNNCON_2HPh)]$ (2). The methanol insoluble product forms purple–green dichroic crystals when recrystallized from dichloromethane layered with methanol in quantitative yield. The infrared spectrum of complex

I II

Fig. 1. Modes of coordination for the phenyl imido moiety.

2 shows features similar to those associated with the organohydrazide ligands found in **1**. The absorptions associated with ν(N–H) occur at 3250 cm^{-1} and ν(N=N) at 1590 cm^{-1}. The carbonyl absorption is not observed, similar to the spectrum of **1**. The technetium-oxo absorption occurs at 950 cm^{-1}.

The positive mode fast atom bombardment mass spectrometric results show the protonated parent ions for both complexes. The mass spectrometric decomposition profiles for these compounds show the generation of a phenylimido containing species for each chelated organohydrazide ligand present in the parent species.

The FAB(+) mass spectrum for complex 1 contains the protonated parent ion of 704 *m*/*z*. A second major peak of 668 *m*/*z* is associated with the loss of the chloride ligand from the parent ion generating $[Tc(NPh)(PhNNCON_2HPh)_2]^+$. Other peaks present correspond to the bis(phenylimido) species $[Tc(NPh)_2(PhNNCON_2HPh)]H^+$ of 520 *m*/*z* and the tris(phenylimido) species $[Tc(NPh)_3]^+$ of 372 *m*/*z*. A peak of 613 *m*/*z* corresponds to the loss of (–NPh) from the parent compound.

The FAB(+) mass spectrum of complex 2 shows the protonated parent ion of $m/z = 825$. The major peak in the decomposition profile is the species associated with the loss of one of the hindered thiolate ligands generating $[TcO(SAr)(PhNNCON_2HPh)]^+$ of 589 *m*/*z*. A peak of 441 *m*/*z* corresponds to the phenylimido containing fragment $[TcO(NPh)(SAr)]^+$.

An X-ray crystallographic structure determination of 2 was undertaken to determine the location of the nitrogen bound proton of the organohydrazide ligand. Positional parameters are shown in Table 1.

The coordination geometry of 2 is intermediate between square pyramidal and trigonal bipyramidal according to the criteria of Muetterties and Guggenberger [18]. The technetium–oxygen distance for the oxo group is 1.658(2) Å which is typical for the Tc(V) oxo complexes [19]. The substituted phenylthiolate ligands form half of the base of the distorted pyramid. The technetium–sulfur bonds for these ligands are 2.2591(8) and 2.2855(7) Å, typical values for Tc(V)–thiolate sulfur bonds [19]. The remaining two coordination sites are occupied by the five-membered chelate ring formed by the 1,2-disubstituted organohydrazines' α-nitrogen and carbonyl-oxygen atoms. The organohydrazide ligand coordinates with the carbonyl group in the site pseudo-*trans* to the oxo group with the O1–Tc–O2 bond angle of 127.5(1)°. An ORTEP diagram showing 15% probability ellipsoids is shown in Fig. 2, with selected atoms labelled. The bonding parameters for the bidentate organohydrazide ligand show multiple bond character throughout (see Tables 2 and 3). This is reflected in the lack of an absorption from the carbonyl moiety in the infrared spectrum. The organohydrazide ligand, including the two phenyl groups, and the technetium atom are essentially coplanar. A planes calculation is listed in Table 4. The N–H proton, which was located on the final fourier map and refined, resides on the β-nitrogen of the exocyclic (–N=N–Ph) unit. The

TABLE 1. Atomic positional parameters for 2

Atom	x	y	z	B_{eq}
Tc1	0.42970(2)	0.18663(2)	0.29212(2)	2.55(1)
S1	0.38104(6)	0.28601(6)	0.18606(6)	3.30(3)
S2	0.27270(5)	0.25125(5)	0.36499(6)	2.95(3)
O1	0.5141(2)	0.2401(2)	0.39741(2)	3.70(9)
O2	0.3956(1)	0.0429(1)	0.2407(2)	3.29(8)
N1	0.5395(2)	0.0827(2)	0.1752(2)	3.2(1)
N2	0.5370(2)	−0.0179(2)	0.1338(2)	3.7(1)
N3	0.4450(2)	−0.1359(2)	0.1301(2)	4.0(1)
N4	0.3670(2)	−0.1508(4)	0.1669(2)	4.1(1)
C11	0.2605(2)	0.3761(2)	0.2198(2)	3.2(1)
C12	0.2558(2)	0.4688(2)	0.3165(3)	3.7(1)
C13	0.1592(3)	0.5353(2)	0.3389(3)	5.0(2)
C14	0.0700(3)	0.5125(3)	0.2683(3)	5.2(2)
C15	0.0791(3)	0.2448(3)	0.1727(3)	4.8(2)
C16	0.1718(2)	0.3521(2)	0.1456(3)	3.6(10)
C21	0.2566(2)	0.1620(2)	0.4240(2)	2.9(1)
C22	0.1796(2)	0.0996(2)	0.3710(2)	3.6(1)
C23	0.1640(3)	0.0321(3)	0.4175(3)	4.7(2)
C24	0.2226(3)	0.0231(3)	0.5135(3)	5.2(2)
C25	0.2959(3)	0.0866(3)	0.5642(3)	4.5(2)
C26	0.3148(2)	0.1563(2)	0.5223(2)	3.3(1)
C30	0.4572(2)	−0.0360(2)	0.1708(2)	3.4(1)
C31	0.6222(2)	0.1086(2)	0.1418(2)	3.5(1)
C32	0.6823(3)	0.0325(3)	0.0582(3)	4.4(1)
C33	0.7627(3)	0.0585(4)	0.0303(3)	5.6(2)
C34	0.7856(3)	0.1584(4)	0.0840(3)	5.6(2)
C35	0.7265(3)	0.2342(3)	0.1671(3)	5.4(2)
C36	0.6441(3)	0.2092(3)	0.1962(3)	4.5(2)
C37	0.3387(3)	−0.2510(3)	0.1249(3)	5.0(2)
C38	0.3898(4)	−0.3347(3)	0.0415(4)	7.1(2)
C39	0.3553(6)	−0.4318(4)	0.0026(6)	10.6(4)
C40	0.2753(8)	−0.4424(5)	0.0445(7)	12.4(5)
C41	0.2269(5)	−0.3578(5)	0.1283(6)	10.5(4)
C42	0.2585(4)	−0.2613(3)	0.1699(4)	7.0(2)
C121	0.3511(3)	0.4999(2)	0.3951(3)	4.7(1)
C122	0.3991(3)	0.5682(3)	0.3591(3)	6.9(2)
C123	0.3311(3)	0.5534(3)	0.5182(3)	7.2(2)
C141	−0.0358(3)	0.5830(4)	0.2985(5)	7.7(2)
C142	−0.0426(4)	0.6942(4)	0.3300(6)	11.9(4)
C143	−0.0840(5)	0.5506(5)	0.3728(6)	12.6(4)
C161	0.1765(3)	0.2533(3)	0.0391(3)	4.8(2)
C162	0.0752(4)	0.2127(3)	−0.0029(4)	7.3(2)
C163	−0.2195(4)	0.2682(4)	−0.0519(3)	8.3(3)
C221	0.1097(2)	0.1114(3)	0.2691(3)	4.2(1)
C222	0.0660(3)	0.0128(3)	0.1917(3)	5.8(2)
C223	0.0237(3)	0.2073(4)	0.3076(4)	6.5(2)
C241	0.2037(5)	−0.0509(4)	0.5649(4)	9.8(4)
C242	0.1894(7)	−0.1496(4)	0.4959(5)	14.6(5)
C243	0.1715(5)	0.0018(4)	0.6738(4)	9.1(3)
C261	0.3969(2)	0.2227(2)	0.5846(3)	3.8(1)
C262	0.3747(3)	0.2919(3)	0.7062(3)	6.5(2)
C263	0.5040(3)	0.1513(3)	0.5826(3)	5.4(2)

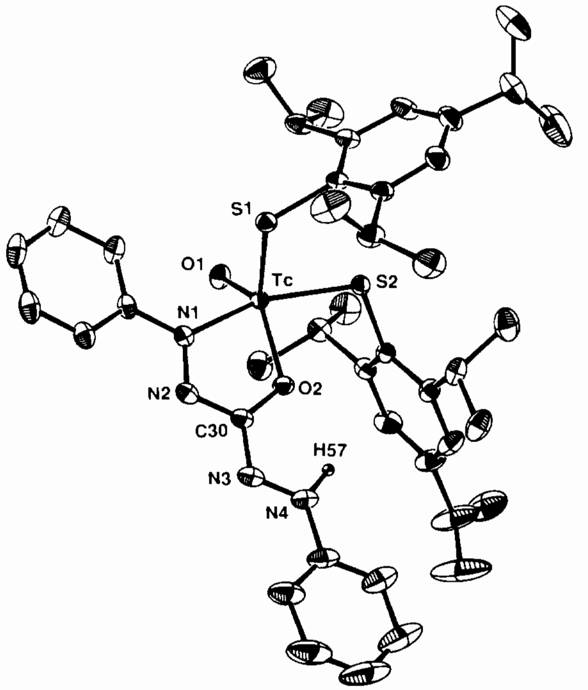

Fig. 2. ORTEP diagram of [$TcO(SC_6H_2Pr^i_3)_2(PhNNCON_2HPh)$] showing 15% probability ellipsoids.

TABLE 2. Bond lengths (A) for **2**

Tc1–O1	1.658(2)	C24–C25	1.379(5)
Tc1–O2	1.990(2)	C24–C241	1.531(5)
Tc1–N1	2.139(2)	C25–C26	1.388(4)
Tc1–S1	2.2591(8)	C26–C261	1.515(4)
Tc1–S2	2.2855(7)	C31–C32	1.390(4)
N1–N2	1.298(3)	C31–C36	1.376(4)
N3–N4	1.315(4)	C32–C33	1.364(5)
O2–C30	1.321(3)	C33–C34	1.371(6)
N2–C30	1.360(4)	C34–C35	1.378(5)
N3–C30	1.321(3)	C35–C36	1.388(5)
N1–C31	1.428(4)	C37–C38	1.369(6)
N4–C37	1.405(4)	C37–C42	1.373(6)
S1–C11	1.790(3)	C38–C39	1.409(6)
S2–C21	1.784(3)	C39–C40	1.35(1)
C11–C12	1.396(4)	C40–C41	1.36(1)
C11–C16	1.406(4)	C41–C42	1.380(6)
C12–C13	1.397(4)	C121–C122	1.524(5)
C12–C121	1.520(4)	C121–C123	1.518(5)
C13–C14	1.389(5)	C141–C142	1.425(7)
C14–C15	1.366(5)	C141–C143	1.514(7)
C14–C141	1.529(5)	C161–C162	1.521(5)
C15–C16	1.386(4)	C161–C163	1.515(6)
C16–C161	1.512(4)	C221–C222	1.524(4)
C21–C22	1.413(4)	C221–C223	1.515(5)
C21–C26	1.401(4)	C241–C242	1.350(6)
C22–C23	1.385(4)	C241–C243	1.404(6)
C22–C221	1.529(4)	C261–C262	1.529(5)
C23–C24	1.393(5)	C261–C263	1.533(5)

TABLE 3. Selected bond angles (°) for **2**

O1–Tc1–O2	127.5(1)	S1–C11–C12	120.4(2)
O1–Tc1–N1	97.3(1)	S1–C11–C16	118.4(2)
O1–Tc1–S1	109.57(8)	S2–C21–C22	117.8(2)
O1–Tc1–S2	104.98(7)	S2–C21–C26	117.8(2)
O2–Tc1–N1	74.35(8)	N1–C31–C32	120.7(3)
O2–Tc1–S1	121.72(6)	N1–C31–C36	119.1(3)
O2–Tc1–S2	86.71(6)	N4–C37–C38	120.5(4)
N1–Tc1–S1	88.93(7)	N4–C37–C42	117.8(4)
N1–Tc1–S2	156.78(7)	N3–N4–H57	111.45
Tc1–N1–N2	117.5(2)	N1–N2–C30	110.5(2)
Tc1–N1–C31	128.1(2)	O2–C30–N3	123.4(3)
Tc1–O2–C30	116.4(2)	C30–N3–N4	114.2(3)
Tc1–S1–C11	112.9(1)	N3–N4–C37	121.1(3)
Tc1–S2–C21	106.6(1)	N2–C30–N3	115.6(3)
S1–Tc1–S2	89.80(3)	N2–C30–O2	121.0(2)
Tc1–N1–N2	117.5(2)	C37–N4–H57	127.3(2)
Tc1–N1–C31	128.1(2)		
Tc1–O2–C30	116.4(2)		
Tc1–S1–C11	112.9(1)		
Tc1–S2–C21	106.6(1)		

TABLE 4. Least-squares plane for **2**

Atoms defining plane	Distance	e.s.d.
Tc1	−0.0036	0.0002
N1	−0.0345	0.0020
N2	0.0306	0.0022
N3	0.0423	0.0023
N4	0.0350	0.0024
O2	−0.0109	0.0017
C30	0.0309	0.0026
C31	−0.0109	0.0027
C32	−0.1417	0.0031
C33	−0.0844	0.0036
C34	0.1011	0.0038
C35	0.2265	0.0035
C36	0.1644	0.0031
C37	−0.0602	0.0033
C38	−0.1962	0.0040
C39	−0.3118	0.0058
C40	−0.3010	0.0076
C41	−0.1497	0.0064
C42	−0.0200	0.0042
H57	0.0627	0.0010

The mean deviation from plane is 0.1013 A.

location of the N–H proton on the exocyclic β-nitrogen has been previously reported in the thio analog of the organohydrazide ligand in the diphenylthiocarbazone molybdenum complex ($(Bu_4N)[MoO_2(PhNNCSN_2Ph)(PhNNCSN_2(H)Ph)]$ [13]. A complete listing of experimental details for the crystallographic studies of complex 2 is given in Table 5.

The similarity of the infrared spectroscopic features associated with the chelating organohydrazide ligands of the structurally characterized, singly-protonated complex 2 and the phenylimido complex 1, along with the similar fragmentation patterns

TABLE 5. X-ray data for structure determination of **2**

Empirical formula	$C_{41}H_{57}N_4O_2S_2Tc$
Formula weight (g mol^{-1})	799.05
Crystal color, habit	purple–green, dichroic block
Crystal dimensions (mm)	0.15 × 0.2 × 0.35
Crystal system	triclinic
a (Å)	13.3613(8)
b (Å)	14.0268(6)
c (Å)	13.0857(6)
α (°)	113.949(4)
β (°)	100.265(4)
γ (°)	76.019(4)
V (Å^3)	2166.0(1)
Space group	$P\bar{1}$ (#2)
Z	2
D(calc.) (g/cm^3)	1.23
D(exp) (g/cm^3)	1.25
μ (cm^{-1})	4.45
Diffractometer	Enraf-Nonius CAD4
Radiation (λ, Å) (graphite monochromated)	Mo Kα(0.71069)
Temperature (°C)	23
No. reflections used in cell determination	25 ($25 < 2\theta < 35°$)
Scan mode	ω–2θ
Scan width (°)	0.84
Scan rate (°/min)	8.0 (in omega)
Max 2θ (°)	55.0
No. reflections measured,	
total	11133
unique	10643
Data collected	$+h\ \pm k\ \pm l$
Reflections collected	$h0l$: $h + l \neq 2n$ $0k0$: $k \neq 2n$
R_{int}	0.50
T_{max}, T_{min}	1.09, 0.91
Correction (Lorentz–polarization)	empirical absorption using DIFABS[a]
Structure solution	direct methods
Refinement	full matrix least-squares
Function minimized	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
Least-squares, wt	$4F_o^2/\sigma^2(F_o^2)$
Atomic scattering factors[b]	neutral scattering factors used throughout
Anomalous dispersion[c]	all non-H atoms
Extinction effects	not observed
Criterion, no. observations	$I > 3\sigma(I)$, 7786
No. variables	469
R, R_w	0.040, 0.045
Goodness of fit	1.50
Max. shift/error in final cycle	0.04
Max. peak in final difference map (e Å^{-3})	0.44
Min. peak in final difference map (e Å^{-3})	−0.60

[a] Ref. 20. [b] Ref. 21. [c] Anomalous dispersion effects were included in F_c [22].

observed in the mass spectrometric results, suggest that the proton associated with organohydrazide ligands in complex **1** is located on the ligands' exocyclic terminal nitrogen as was noted previously for the structurally characterized molybdenum diphenylthiocarbazone complex.

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