Table III. Bond Lengths and Selected Bond Angles[a]

Bond Lengths, Å			
Au-N(1)	1.972 (17)	C(5)-C(6)	1.435 (32)
Au-N(4)	1.962 (3)	C(6)-C(7)	1.322 (33)
Au-N(8)	1.991 (4)	C(12)-C(13)	1.338 (22)
Au-N(11)	1.975 (16)	C(13)-C(14)	1.410 (30)
N(1)-C(14)	1.350 (25)	C(2)-C(3)	1.436 (30)
N(4)-C(5)	1.298 (20)	C(9)-C(10)	1.329 (27)
N(8)-C(7)	1.288 (23)	C(5)-C(5′)	1.529 (32)
N(11)-C(12)	1.356 (16)	C(7)-C(7′)	1.592 (20)
N(1)-C(2)	1.421 (28)	C(12)-C(12′)	1.534 (24)
N(4)-C(3)	1.517 (22)	C(14)-C(14′)	1.544 (26)
N(8)-C(9)	1.363 (22)	B-F(1-4)	1.285 (35), 1.293 (27), 1.353 (25), 1.393 (43)
N(11)-C(10)	1.393 (23)		

Bond Angles, Deg			
N(1)-Au-N(4)	83.6 (5)	C(12)-C(13)-C(14)	129.6 (17)
N(4)-Au-N(8)	95.5 (1)	N(8)-C(9)-C(10)	118.5 (15)
N(8)-Au-N(11)	84.2 (4)	N(11)-C(10)-C(9)	119.2 (17)
N(11)-Au-N(1)	96.8 (6)	N(1)-C(2)-C(3)	112.8 (19)
N(1)-C(14)-C(13)	125.2 (17)	N(4)-C(3)-C(2)	107.9 (16)
N(4)-C(5)-C(6)	123.6 (18)	C(3)-N(4)-C(5)	123.8 (13)
N(8)-C(7)-C(6)	128.6 (19)	C(2)-N(1)-C(14)	125.4 (18)
N(11)-C(12)-C(13)	124.8 (11)	C(9)-N(8)-C(7)	129.5 (12)
C(5)-C(6)-C(7)	127.5 (19)	C(10)-N(11)-C(12)	128.9 (14)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

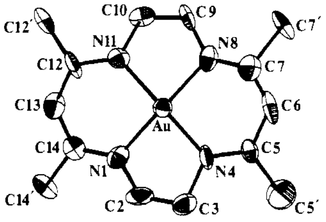

Figure 1. ORTEP drawing of cation II. Thermal ellipsoids are shown at the 50% level.

bridge. The methyl carbons are all within 0.08–0.16 Å of the least-squares plane. The presence of a double bond in one of the five-membered rings is clearly evident from the C(9)–C(10) bond distance of 1.329 (27) Å. Bond distances in the BF_4^- anion vary over a ~0.1 Å range and are shorter than expected.[8] Also the bond angles vary from 102 (2) to 115 (2)°. These deviations from ideal T_d point group symmetry are attributed to the relatively high thermal parameters found for the fluorines.[9]

It is of interest to compare the structural parameters of cation II with those found previously for I. In both complexes, C$\overset{\cdots}{-}$N distances within the *same* β-diiminate ring differ by no more than 0.01 (4) Å. However they differ by as much as 0.07 (4) Å between the two inequivalent β-diiminate rings of II. In one ring, C$\overset{\cdots}{-}$N distances are comparable to those found in I (1.340 (8) Å, average), whereas in the other ring these distances are very close to those found for a β-diimine complex having localized imine double bonds (1.263 (6)–1.282 (7) Å).[10]

The two C$\overset{\cdots}{-}$C distances in I differ only slightly (1.370 (10) and 1.411 (10) Å). In II, on the other hand, differences in the C$\overset{\cdots}{-}$C bond lengths within each β-diiminate ring are significantly greater. This would imply a smaller degree of π delocalization in II; however, the equivalency of C$\overset{\cdots}{-}$N bonds within each ring rules out a structure with alternating double and single bonds. It appears that the presence of the double bond in one of the five-membered rings of II places a steric constraint on the entire macrocycle such that bond lengths cannot be readily interpreted by simple valence-bond considerations.

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Registry No. II, 71393-59-4.

Supplementary Material Available: Table IV containing anisotropic thermal parameters and Table V with observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[8] MacGillavry, C. H., Rieck, G. D., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III, p 262.

[9] Final isotropic thermal parameters for fluorines are as follows: F(1), 11.272 (646); F(2), 15.925 (1025); F(3), 19.922 (1384); F(4), 11.399 (639).

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Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027

Structure of a Homoleptic Seven-Coordinate Molybdenum(II) Aryl Isocyanide Complex $[Mo(CNPh)_7](PF_6)_2$[1,2]

John C. Dewan and Stephen J. Lippard*

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Although the structures of numerous seven-coordinate alkyl isocyanide complexes of divalent group 6 transition metals have been crystallographically determined both in our laboratory[2,3] and in others,[4] no aryl isocyanide complexes have thus far been studied. Recently, homoleptic seven-coordinate aryl isocyanide complexes of Mo(II) and W(II) have become available through the synthetic efforts of Walton and co-workers.[5] A structural study of one of these, $[Mo(CNPh)_7](PF_6)_2$, was therefore undertaken to confirm the proposed coordination number and to provide bond length and angle data for comparison with the known alkyl isocyanide analogues.

Experimental Section

Collection and Reduction of X-ray Data. The synthesis and crystallization of $[Mo(CNPh)_7](PF_6)_2$ have been described previously.[5] The yellow crystal used in the diffraction study had approximate dimensions 0.27 mm × 0.07 mm × 0.47 mm and was sealed in a capillary to minimize decomposition. Study of the compound on the diffractometer showed only $\bar{1}$ Laue symmetry and no systematic absences, indicating either space group $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2).[6] A systematic search using TRACER-II[7] failed to reveal any higher

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[1] Part 17 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 16 see ref 2.

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Table I. Crystal Parameters at 25 °C of $[Mo(CNPh)_7](PF_6)_2$[a]

$a = 14.726$ (2) Å	$V = 2507.8$ Å^3
$b = 16.543$ (4) Å	mol wt = 1107.7
$c = 10.499$ (3) Å	space group = $P\bar{1}$
$\alpha = 91.41$ (2)°	$Z = 2$
$\beta = 94.78$ (2)°	ρ(calcd) = 1.467 g cm^{-3}
$\gamma = 79.72$ (2)°	ρ(obsd)[b] = 1.47 (1) g cm^{-3}

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30°$. [b] By suspension in a mixture of CCl_4 and $CHCl_3$.

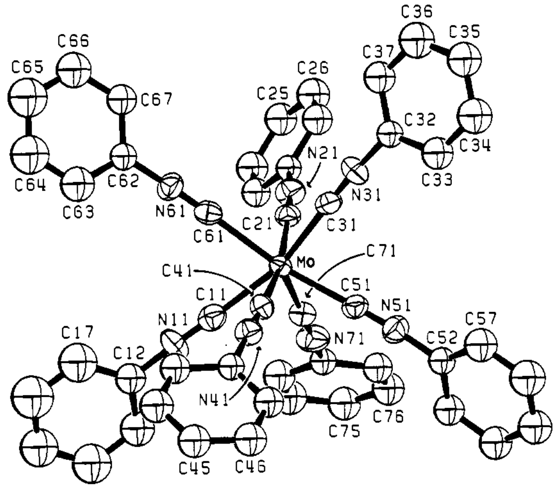

Figure 1. Structure of the $[Mo(CNPh)_7]^{2+}$ cation showing the atom labeling scheme and 40% probability thermal ellipsoids. Hydrogen atoms and some of the phenyl carbon atom labels are omitted for clarity.

symmetry, and the structure has been successfully solved and refined in the centrosymmetric space group $P\bar{1}$. Open-counter ω scans of several strong low-angle reflections showed the crystal quality to be acceptable ($\Delta\bar{\omega}_{1/2} = 0.10°$). Crystal parameters are given in Table I. Data collection and reduction procedures were similar to those described in ref 8. A total of 8813 unique ($\pm h,\pm k,+l$) reflections in the range $3° \leq 2\theta \leq 50°$ were collected. Because of the small linear-absorption coefficient (4 cm^{-1}) and narrow estimated range of transmission factors (0.90–0.97), an absorption correction was not applied.

Determination and Refinement of the Structure. The structure was solved by the heavy-atom method using SHELX-76.[9] Because of a limitation on the number of atoms that SHELX-76 can handle, final full-matrix least-squares refinement was carried out by using the system of programs consisting of CUGLS, RBANG, FOURIER, and ORFFE[10] adapted to a VAX-11/780 computer. Neutral-atom scattering factors and anomalous dispersion corrections for the nonhydrogen atoms were taken from ref 11 while hydrogen atom scattering factors were those of Stewart et al.[12] The seven phenyl rings of the cation, including hydrogen atoms, were refined as rigid groups with C–C = 1.392 Å, C–H = 0.96 Å, and C–C–C = C–C–H = 120°. With use of 3965 unique reflections with $F^2 > 3\sigma(F^2)$, the structure was refined with 346 variable parameters. The final values for R_1 and R_2 were 0.066 and 0.074, respectively, and the goodness of fit (GOF) value was 1.755.[13] In the final cycle of least-squares refinement the maximum Δ/σ was 0.02 and a final difference Fourier map showed no peak greater than 1 e Å^{-3}.

Table II. Final Positional Parameters for the Nonhydrogen Atoms of $[Mo(CNPh)_7](PF_6)_2$[a,b]

atom	x	y	z
Mo	0.18576(6)	0.22023(5)	0.39469(8)
P(1)	0.1928(2)	0.2220(2)	0.8782(3)
P(2)	0.2504(3)	-0.2459(2)	0.5362(3)
F(11)	0.1363(4)	0.1729(3)	0.9628(5)
F(12)	0.1635(4)	0.3025(4)	0.9634(6)
F(13)	0.2482(5)	0.2712(5)	0.7946(6)
F(14)	0.2832(4)	0.1945(4)	0.9733(6)
F(15)	0.1018(4)	0.2481(4)	0.7852(5)
F(16)	0.2214(4)	0.1409(4)	0.7947(6)
F(21)	0.2524(7)	-0.2179(6)	0.6780(8)
F(22)	0.2472(7)	-0.2747(7)	0.3969(8)
F(23)	0.2378(8)	-0.1546(6)	0.5003(11)
F(24)	0.3560(6)	-0.2550(7)	0.5391(11)
F(25)	0.1450(6)	-0.2393(6)	0.5365(11)
F(26)	0.2624(7)	-0.3369(5)	0.5766(10)
N(11)	0.3407(6)	0.0964(5)	0.5665(8)
N(21)	0.3094(6)	0.3014(5)	0.2074(7)
N(31)	0.0055(6)	0.2782(5)	0.1871(8)
N(41)	0.0774(5)	0.1087(5)	0.5630(8)
N(51)	0.0517(6)	0.3582(5)	0.5495(8)
N(61)	0.2386(5)	0.0554(5)	0.2104(7)
N(71)	0.3157(6)	0.3321(5)	0.5464(8)
C(11)	0.2875(7)	0.1416(6)	0.5078(9)
C(12)	0.4005(6)	0.0429(5)	0.6426(7)
C(13)	0.4427(7)	0.0704(4)	0.7550(7)
C(14)	0.5054(5)	0.0154(6)	0.8315(6)
C(15)	0.5259(7)	-0.0670(5)	0.7957(8)
C(16)	0.4837(8)	-0.0944(4)	0.6833(9)
C(17)	0.4210(5)	-0.0394(5)	0.6068(7)
C(21)	0.2614(7)	0.2728(6)	0.2672(9)
C(22)	0.3753(4)	0.3304(5)	0.1444(6)
C(23)	0.4675(5)	0.3129(3)	0.1926(5)
C(24)	0.5355(3)	0.3392(5)	0.1281(6)
C(25)	0.5114(4)	0.3831(6)	0.0153(6)
C(26)	0.4192(5)	0.4006(4)	-0.0330(5)
C(27)	0.3511(3)	0.3742(5)	0.0315(6)
C(31)	0.0700(7)	0.2583(6)	0.2569(9)
C(32)	-0.0709(5)	0.3082(8)	0.1080(6)
C(33)	-0.1473(5)	0.3562(4)	0.1583(5)
C(34)	-0.2234(5)	0.3905(6)	0.0774(7)
C(35)	-0.2231(5)	0.3767(8)	-0.0539(7)
C(36)	-0.1467(5)	0.3287(5)	-0.1042(5)
C(37)	-0.0705(5)	0.2944(6)	-0.0233(6)
C(41)	0.1088(6)	0.1488(6)	0.4991(9)
C(42)	0.0462(5)	0.0599(4)	0.6481(5)
C(43)	0.0811(4)	-0.0240(4)	0.6521(6)
C(44)	0.0538(5)	-0.0726(3)	0.7432(7)
C(45)	-0.0083(6)	-0.0372(4)	0.8303(6)
C(46)	-0.0431(4)	0.0467(4)	0.8263(6)
C(47)	-0.0159(5)	0.0952(3)	0.7352(6)
C(51)	0.0991(7)	0.3100(6)	0.4938(9)
C(52)	0.0003(5)	0.4146(4)	0.6256(6)
C(53)	0.0452(4)	0.4443(5)	0.7340(6)
C(54)	-0.0042(5)	0.5016(4)	0.8134(5)
C(55)	-0.0984(5)	0.5291(5)	0.7845(6)
C(56)	-0.1433(4)	0.4994(5)	0.6761(7)
C(57)	-0.0939(5)	0.4421(4)	0.5966(6)
C(61)	0.2202(6)	0.1126(6)	0.2705(9)
C(62)	0.2608(11)	-0.0152(4)	0.1412(6)
C(63)	0.2821(5)	-0.0893(5)	0.2061(5)
C(64)	0.3014(9)	-0.1629(4)	0.1383(8)
C(65)	0.2994(11)	-0.1623(4)	0.0055(8)
C(66)	0.2782(5)	-0.0881(5)	-0.0593(5)
C(67)	0.2588(8)	-0.0146(4)	0.0085(6)
C(71)	0.2672(7)	0.2928(6)	0.4954(9)
C(72)	0.3810(4)	0.3779(4)	0.5922(6)
C(73)	0.4729(5)	0.3408(3)	0.6193(7)
C(74)	0.5389(4)	0.3884(4)	0.6603(7)
C(75)	0.5131(4)	0.4730(4)	0.6742(7)
C(76)	0.4213(5)	0.5101(3)	0.6471(7)
C(77)	0.3552(4)	0.4626(4)	0.6061(6)

[a] Atoms of the cation are labeled as shown in Figure 1. For the anions, F(11)–F(16) are bound to P(1) and F(21)–F(26) are bound to P(2). Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter. [b] Parameters for the phenyl ring carbon atoms were derived from the rigid-group parameters (see: Gill, J. T.; Mayerle, J. J.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. *Inorg. Chem.* 1976, *15*, 1155).

Results

Final nonhydrogen atom positional parameters appear in Table II and interatomic distances and angles in Table III. Observed and calculated structure factors, thermal parameters, and hydrogen atom positional parameters are available as supplementary material in Tables S1–S3, respectively. Figure

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(13) $R_1 = \sum|\Delta|/\sum|F_o|$, $R_2 = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$, and GOF = $[\sum w\Delta^2/(NO - NV)]^{1/2}$, where $\Delta = |F_o| - |F_c|$, NO = number of observed data, and NV = number of variables.

Table III. Interatomic Distances (Å) and Angles (Deg) for $[Mo(CNPh)_7](PF_6)_2$[a]

	Coordination Sphere[b]		
Mo-C(71)	2.059(11)	Mo-C(41)	2.152(11)
Mo-C(51)	2.094(9)	Mo-C(31)	2.156(9)
Mo-C(11)	2.105(10)	Mo-C(61)	2.191(10)
Mo-C(21)	2.107(10)		
C(21)-Mo-C(41)	169.5(4)	C(31)-Mo-C(61)	86.0(3)
C(11)-Mo-C(31)	159.2(4)	C(21)-Mo-C(31)	84.4(4)
C(51)-Mo-C(61)	156.2(4)	C(21)-Mo-C(61)	82.1(4)
C(61)-Mo-C(71)	131.9(4)	C(41)-Mo-C(51)	77.1(4)
C(31)-Mo-C(71)	127.9(4)	C(11)-Mo-C(61)	76.7(4)
C(41)-Mo-C(71)	118.7(4)	C(31)-Mo-C(51)	76.7(3)
C(11)-Mo-C(51)	115.9(4)	C(11)-Mo-C(41)	75.5(4)
C(21)-Mo-C(51)	111.8(4)	C(11)-Mo-C(71)	72.8(4)
C(11)-Mo-C(21)	104.2(4)	C(51)-Mo-C(71)	71.9(4)
C(31)-Mo-C(41)	92.5(4)	C(21)-Mo-C(71)	70.6(4)
C(41)-Mo-C(61)	87.6(4)		
	Ligand Geometry[c]		
C(11)-N(11)	1.133(12)	N(11)-C(12)	1.355(11)
C(21)-N(21)	1.152(14)	N(21)-C(22)	1.378(12)
C(31)-N(31)	1.153(12)	N(31)-C(32)	1.367(10)
C(41)-N(41)	1.134(14)	N(41)-C(42)	1.378(11)
C(51)-N(51)	1.146(12)	N(51)-C(52)	1.376(10)
C(61)-N(61)	1.129(12)	N(61)-C(62)	1.363(10)
C(71)-N(71)	1.142(14)	N(71)-C(72)	1.376(12)
Mo-C(11)-N(11)	177.0(9)	C(11)-N(11)-C(12)	176.4(11)
Mo-C(21)-N(21)	173.2(8)	C(21)-N(21)-C(22)	173.3(8)
Mo-C(31)-N(31)	177.1(9)	C(31)-N(31)-C(32)	175.3(10)
Mo-C(41)-N(41)	172.0(8)	C(41)-N(41)-C(42)	174.9(9)
Mo-C(51)-N(51)	178.9(9)	C(51)-N(51)-C(52)	174.9(9)
Mo-C(61)-N(61)	177.5(8)	C(61)-N(61)-C(62)	178.2(10)
Mo-C(71)-N(71)	176.3(9)	C(71)-N(71)-C(72)	171.8(10)
	Anion Geometry		
min P-F	1.526(9)	mean *cis* F-P-F	90.0(5)
max P-F	1.601(7)	min *trans* F-P-F	178.1(6)
mean P-F	1.566(8)	max *trans* F-P-F	179.5(4)
min *cis* F-P-F	87.6(6)	mean *trans* F-P-F	178.8(5)
max *cis* F-P-F	93.1(6)		

[a] See footnote *a*, Table II. Distances have not been corrected for thermal motion. Standard deviations, quoted for mean values, are the average of the standard deviation for the individual values. [b] Distances and angles at the metal are listed in increasing and decreasing size, respectively. [c] Phenyl rings were refined as rigid groups; see text.

1 shows the geometry of the cation along with the atom labeling scheme.

Discussion

The structure consists of discrete $[Mo(CNPh)_7]^{2+}$ cations and PF_6^- anions having no crystallographically imposed symmetry. The geometry of the anions is normal. The cations are seven-coordinate, confirming the original assignment.[5a] Their geometry approximates that of the 4:3 (C_s) piano stool structure recently identified in several related alkyl isocyanide Mo(II) and W(II) complexes.[3,4] This choice of geometry is made by comparing the C–Mo–C interbond angles of Table III with those tabulated[3g] for various reference geometries. In this description the quadrilateral face is defined by atoms C(11), C(41), C(51), and C(71) and the trigonal face by atoms C(21), C(31), and C(61) (Figure 1). After the bond lengths were normalized, the dihedral angle between the quadrilateral and trigonal faces was computed to be 1.04° while that across the diagonal of the quadrilateral face was found to be 2.58°. These values confirm the 4:3 (C_s) piano stool to be a good reference geometry.[3e,g] Alternatively, the structure may be referenced to an idealized C_{3v} capped octahedron with C(71) the capping (c) atom, C(11), C(21), and C(51) comprising the capped face (cf), and C(31), C(41), C(61) constituting the uncapped face (uf). With this latter reference geometry the familiar[4a,3h,3j] 1:3:3 bond length pattern emerges: $Mo–C_c$, 2.059 (11) Å; $Mo–C_{cf}$, 2.102 (average) Å; $Mo–C_{uf}$, 2.166 (average) Å. Similar results were found for the related seven-coordinate homoleptic cations $[Cr(CN\text{-}t\text{-}Bu)_7]^{2+}$ [3j] and $[Mo(CNMe)_7]^{2+}$.[4a]

The mean Mo–C bond length of 2.123 ± 0.04 Å in the $[Mo(CNPh)_7]^{2+}$ cation is essentially the same as the corresponding mean distances in $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$ (2.115 ± 0.04 Å),[3b] $[Mo(CNMe)_7]^{2+}$ (2.107 ± 0.04 Å),[4a] and $[Mo(CN\text{-}c\text{-}C_6H_{11})_7]^{2+}$ (2.106 ± 0.04 Å).[3h] The internal geometry of the phenyl isocyanide ligands is summarized in Table III.

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Supplementary Material Available: Tables S1–S3 reporting respectively final observed and calculated structure factors, final thermal parameters for the nonhydrogen atoms, and fixed hydrogen atom positional and isotropic thermal parameters (20 pages). Ordering information is given on any current masthead page.

Contribution from the Structural Chemistry Group,
Department of Chemistry, Indian Institute of Technology,
Madras 600036, India

^{61}Ni Hyperfine Interactions in Dichlorobis[*o*-phenylenebis(dimethylphosphine)]nickel(III) Perchlorate, $[Ni(phmp)_2Cl_2]ClO_4$

E. Balasivasubramanian, C. N. Sethulekshmi,
and P. T. Manoharan*

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There are only a few instances[1-7] of EPR studies of low-spin nickel complexes that also give information on the metal hyperfine interaction. There are still fewer systems[6,7] that provide ligand hyperfine interaction from all the bonded ligand nuclei, in addition to the metal hyperfine interaction due to ^{61}Ni, to enable us to obtain a complete picture of the unpaired electron distribution in the complex. Detailed EPR studies of Ni(III) in the ligand environment of group 5B donors have revealed a highly delocalized wave function for the unpaired electron.[6,8-10]

An earlier analysis[10] of ligand hyperfine interaction by a single-crystal EPR study of $[Ni(phmp)_2Cl_2]ClO_4$ [where phmp is *o*-phenylenebis(dimethylphosphine)] revealed delocalization amounting to 68% of the unpaired spin density on the ligand nuclei. The present investigation on the d^7 low-spin nickel(III) complex enriched with 85% nickel-61 isotope is an attempt to have a critical look at this estimate on the basis of the ^{61}Ni hyperfine coupling tensor.

Experimental Section

The complexes $[Ni(phmp)_2Cl_2]ClO_4$ and $[Co(phmp)_2Cl_2]ClO_4$ were prepared according to the procedure reported earlier.[11] The nickel(III) complex enriched with the magnetic isotope ^{61}Ni was made with 85% isotopically pure NiO. A 1:1 mixture of acetonitrile and absolute alcohol was used for solution EPR measurements.

Single-crystal EPR measurements were made on $[^{61}Ni(phmp)_2Cl_2]^+$ magnetically diluted with the corresponding diamagnetic [Co-

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